

# SAXS studies in Chemical and Materials Science

SAS Short Course  
“Beyond  $R_G$ ”  
Advanced Photon Source  
2013

**Sungsik Lee**

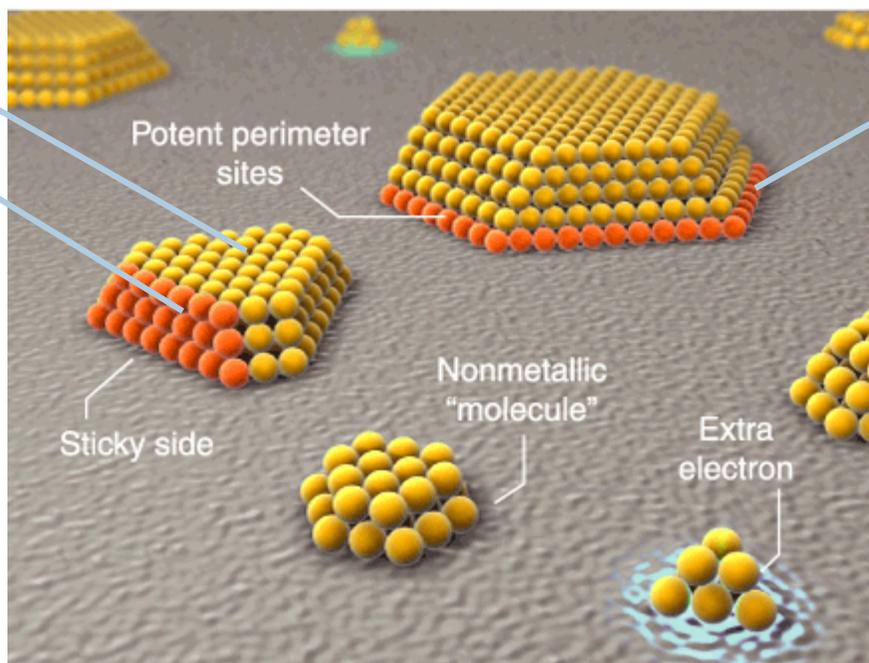
Chemical and Materials Science group

X-ray Science Division

Advanced Photon Source

# Catalysts Size effect

Surface area dependent

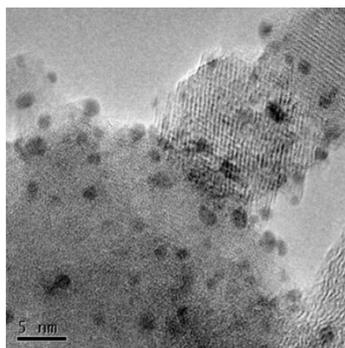
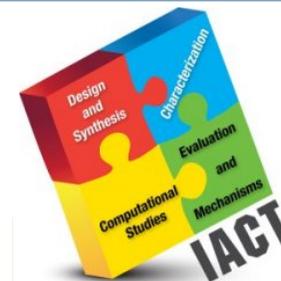


Particle size dependent

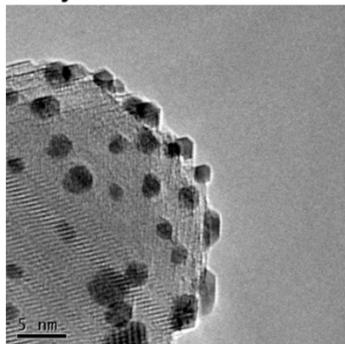
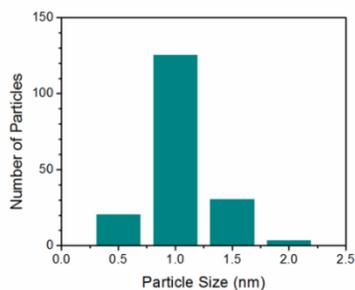
Using SAXS to study catalysts in real time and in-situ condition



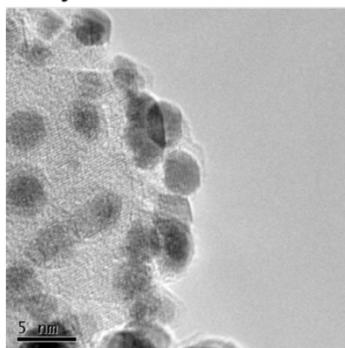
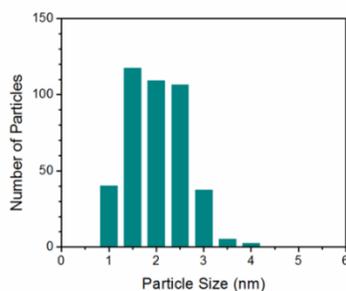
# SAXS: size and size distribution information



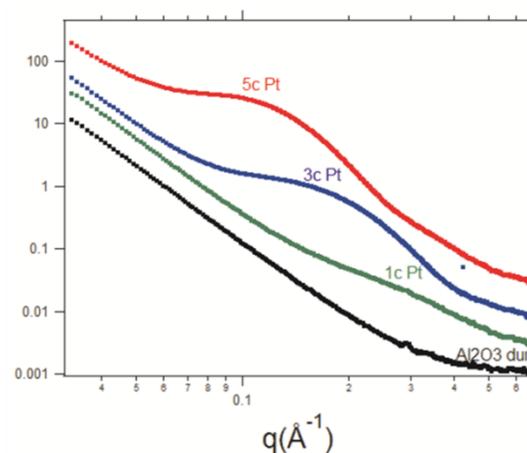
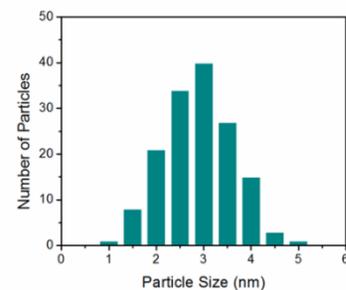
1 cycle Pt on alumina



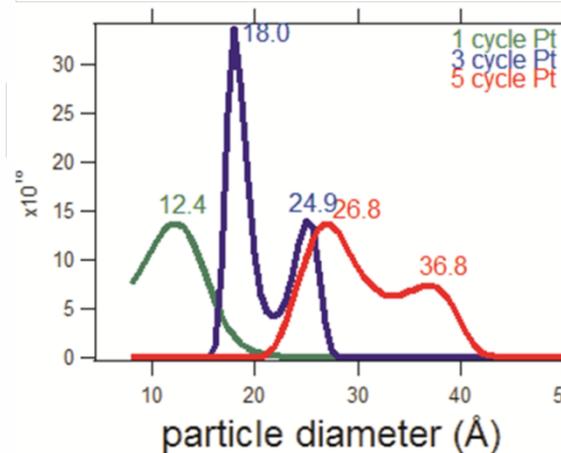
3 cycle Pt on alumina



5 cycle Pt on alumina



SAXS fitting



## Operando Catalysis Studies

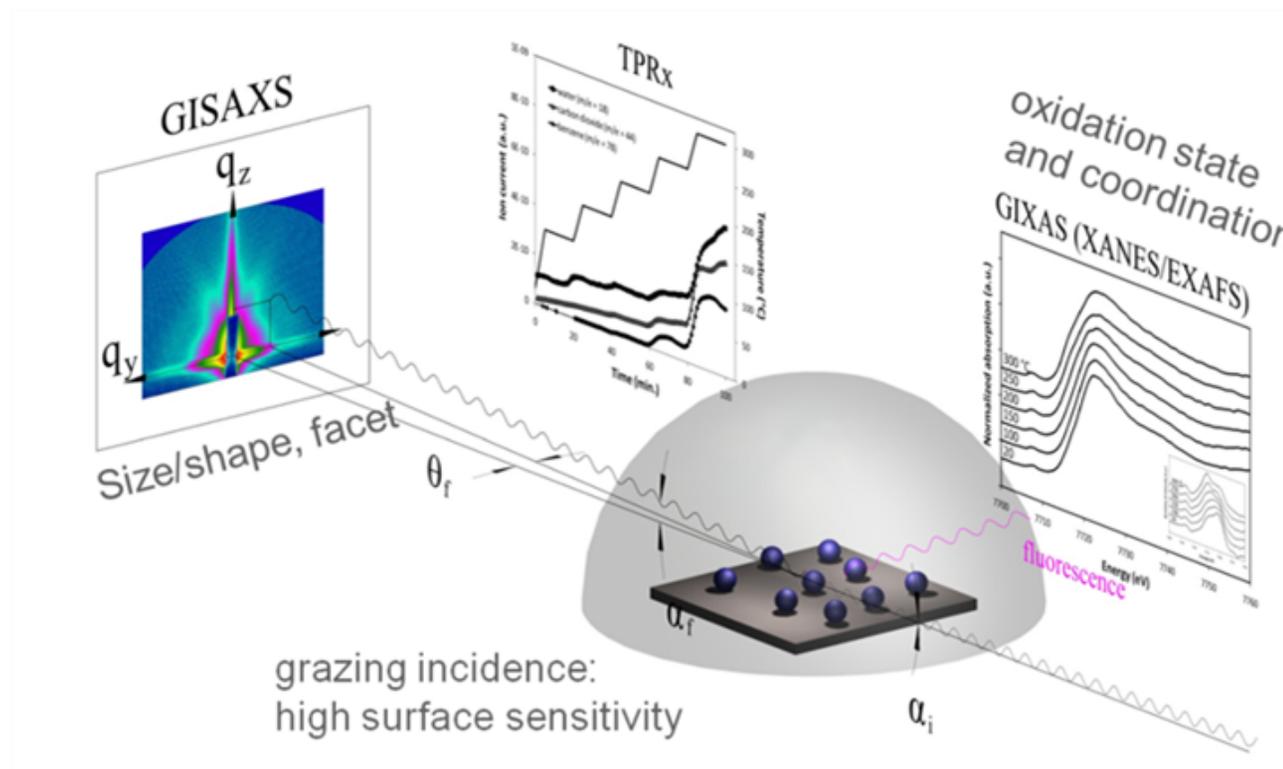
**Small angle scattering and spectroscopy *in situ*, time resolved methods along with mass spectrometry are being applied to catalysis research:**

- This program is studying selective oxidations, oxidative decomposition, Fischer-Tropsch synthesis(FTS), hydrogenation and dehydrogenation of hydrocarbons.
- Size selected metal clusters landed on various atomic layer deposition(ALD) prepared surfaces are being used in these experiments



# 12ID-C setup

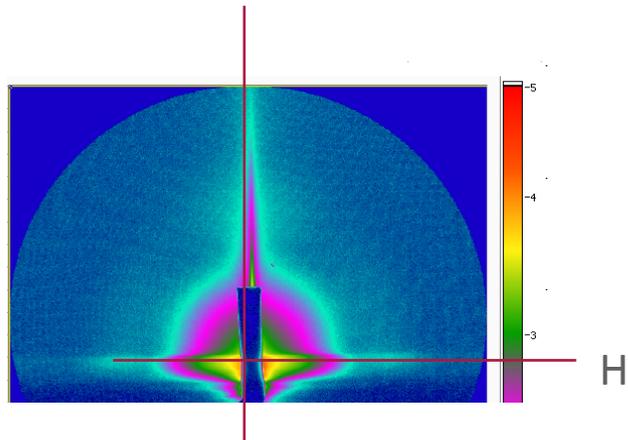
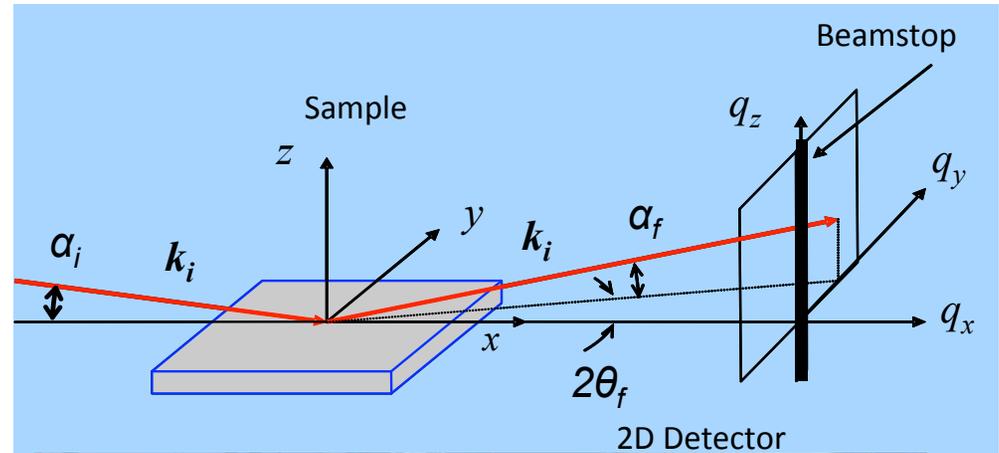
- Energy range: 4.5 – 45 keV
- Flux:  $1 \times 10^{13}$  (photons/sec) at 10 keV
- Techniques
  - SAXS
  - ASAXS
  - GISAXS
  - WAXS
  - GIXAS



# Approach - In situ grazing incidence SAXS

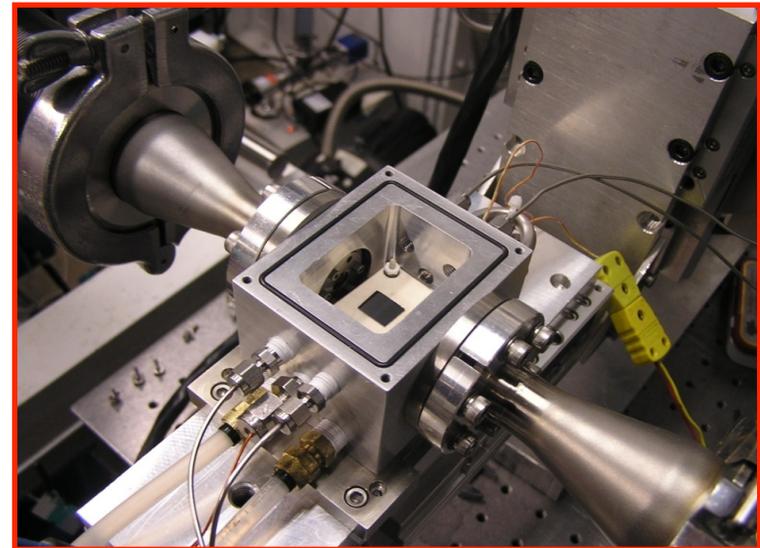
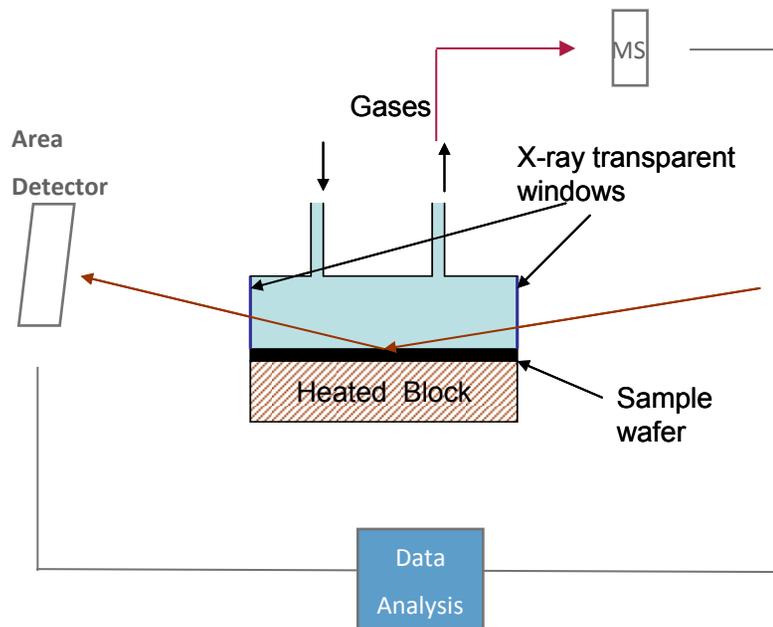
## Grazing Incidence SAXS (GISAXS)

- Study particles and clusters on surfaces
- All information from regular SAXS plus
  - depth information
  - particle distribution
  - orientation relative to the surface
- *In situ* heat, pressure



# In Situ GISAXS Cell

- Small volume cell to reduce scattering from gases, attached to goniometer within in a larger vacuum chamber
- Products monitored by online MS



# In Situ GISAXS Cell

## Nanoparticle growth

1. Kim, M. H.; Lee, B.; Lee, S.; Larson, C.; Baik, J. M.; Yavuz, C. T.; Seifert, S.; Vajda, S.; Winans, R. E.; Moskovits, M.; Stucky, G. D.; Wodtke, A. M., *Nano Letters* 2009, 9 (12), 4138-4146.
2. Vajda, S.; Lee, S.; Sell, K.; Barke, I.; Kleibert, A.; Oeynhausen, V. v.; Meiwes-Broer, K.-H.; Rodríguez, A. F.; Elam, J. W.; Pellin, M. M.; Lee, B.; Seifert, S.; Winans, R. E., *J. Chem. Phys.* 2009, 131 (2), 121104.
3. Liu, C.; Lee, S.; Su, D.; Lee, B.; Lee, S.; Yin, C.; Vajda, S.; Pfefferle, L.; Haller, G. L., *Langmuir* 2012, 28 (49), 17159-17167.
4. Ferguson, G.; Yin, C.; Kwan, G.; Tyo, E.; Lee, S.; Greeley, J.; Zapol, P.; Lee, B.; Seifert, S.; Winans, R.; Vajda, S.; Curtiss, L. A., *J. Phys. Chem. C* 2012, 116 (45), 24027-24034.
5. Yin, F.; Lee, S.; Abdela, A.; Vajda, S.; Palmer, R. E., *J. Chem. Phys.* 2011, 134 (14), 141101.
6. Winans, R. E.; Vajda, S.; Ballentine, G. E.; Elam, J. W.; Lee, B.; Pellin, M. J.; Seifert, S.; Tikhonov, G. Y.; Tomczyk, N. A., *Top. Catal.* 2006, 39 (3-4), 145-149.
7. Vajda, S.; Winans, R. E.; Elam, J. W.; Lee, B.; Pellin, M. J.; Seifert, S.; Tikhonov, G. Y.; Tomczyk, N. A., *Top. Catal.* 2006, 39 (3-4), 161-166.
8. Lee, B.; Seifert, S.; Riley, S. J.; Tikhonov, G.; Tomczyk, N. A.; Vajda, S.; Winans, R. E. *J. Chem. Phys.* 2005, 123, 74701.

## Propylene epoxydation

1. Lee, S.; Molina, Luis M.; López, María J.; Alonso, Julio A.; Hammer, B.; Lee, B.; Seifert, S.; Winans, Randall E.; Elam, Jeffrey W.; Pellin, Michael J.; Vajda, S., *Angew. Chem. Int. Ed.* 2009, 48 (8), 1467-1471.
2. Lei, Y.; Mehmood, F.; Lee, S.; Greeley, J.; Lee, B.; Seifert, S.; Winans, R. E.; Elam, J. W.; Meyer, R. J.; Redfern, P. C.; Teschner, D.; Schlogl, R.; Pellin, M. J.; Curtiss, L. A.; Vajda, S., *Science* 2010, 328 (5975), 224-228.
3. Molina, L. M.; Lee, S.; Sell, K.; Barcaro, G.; Fortunelli, A.; Lee, B.; Seifert, S.; Winans, R. E.; Elam, J. W.; Pellin, M. J.; Barke, I.; Oeynhausen, V. v.; Lei, Y.; Meyer, R. J.; Alonso, J. A.; Fraile-Rodríguez, A.; Kleibert, A.; Giorgio, S.; Henry, C. R.; Meiwes-Broer, K.-H.; Vajda, S., *Catal. Today* 2011, 160 (1), 116-130

## Cyclohexane/cyclohexene dehydrogenation

1. Tyo, E. C.; Yin, C.; Vece, M. D.; Qian, Q.; Kwon, G.; Lee, S.; Lee, B.; DeBartolo, J. E.; Seifert, S.; Winans, R. E.; Si, R.; Ricks, B.; Goergen, S.; Rutter, M.; Zugic, B.; Flytzani-Stephanopoulos, M.; Wang, Z.; Palmer, R. E.; Neurock, M.; Vajda, S., *ACS Catal.* 2012, 2 (11), 2409-2423.
2. Lee, S.; Vece, M. D.; Lee, B.; Seifert, S.; Winans, R. E.; Vajda, S., *ChemCatChem* 2012, 4 (10), 1632-1637.
3. Lee, S.; Vece, M. D.; Lee, B.; Seifert, S.; Winans, R. E.; Vajda, S., *Phys. Chem. Chem. Phys.* 2012, 14, 9336-9342.

## Ethylene hydrogenation

1. Wyrzgol, S. A.; Schafer, S.; Lee, S.; Lee, B.; Di Vece, M.; Li, X.; Seifert, S.; Winans, R. E.; Stutzmann, M.; Lercher, J. A.; Vajda, S., *Phys. Chem. Chem. Phys.* 2010, 12 (21), 5585-95.

## Methanol decomposition

1. Lee, S.; Lee, B.; Mehmood, F.; Seifert, S.; Libera, J. A.; Elam, J. W.; Greeley, J.; Zapol, P.; Curtiss, L. A.; Pellin, M. J.; Stair, P. C.; Winans, R. E.; Vajda, S., *J. Phys. Chem. C* 2010, 114 (23), 10342-10348.



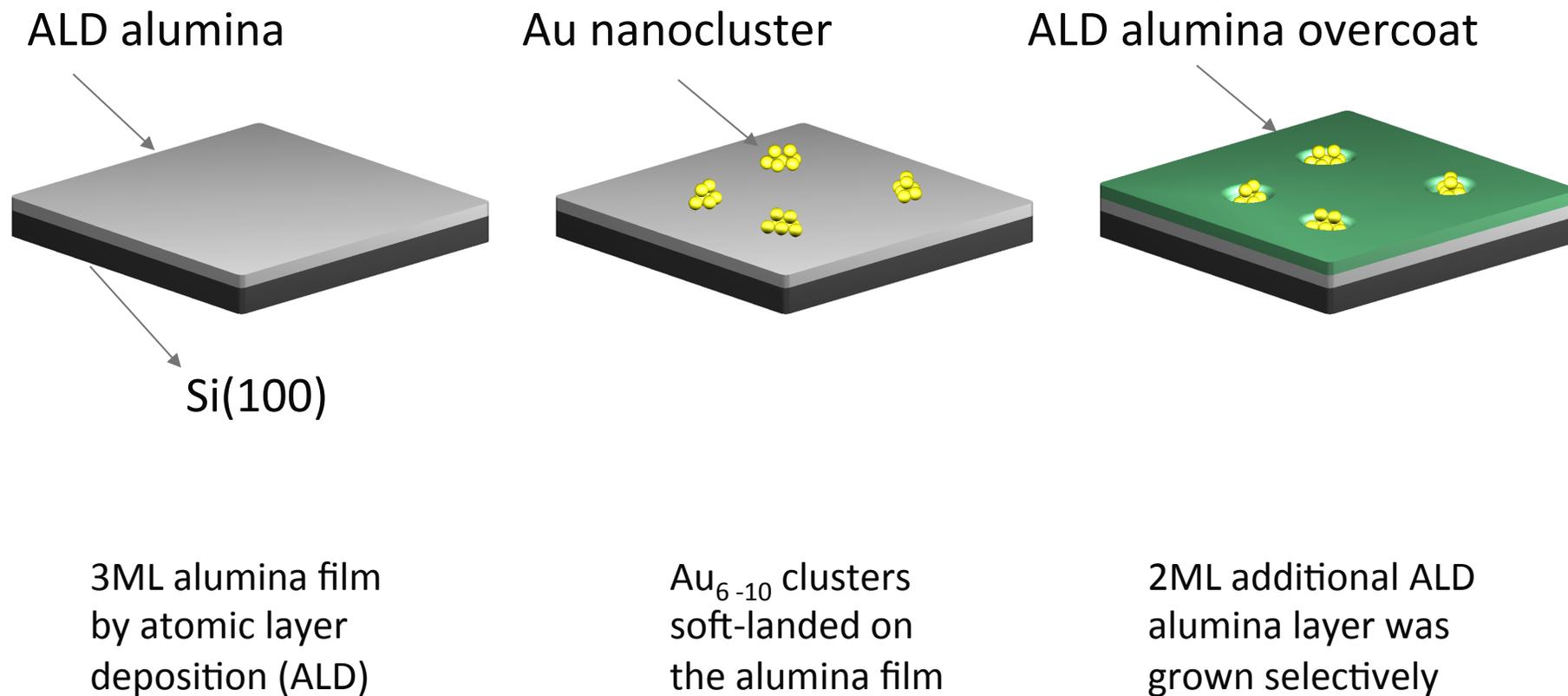


## Sintering resistant nanoparticle

- Possible to control metal catalyst size by atomic scale
- There are various techniques available
  - Size selected cluster deposition
  - ALD(atomic layer deposition)
  - Dendrimer or DNA modified nanoparticles
- It is important to understand how nanoparticles behave at high temperature and reaction condition
- How to prevent sintering?

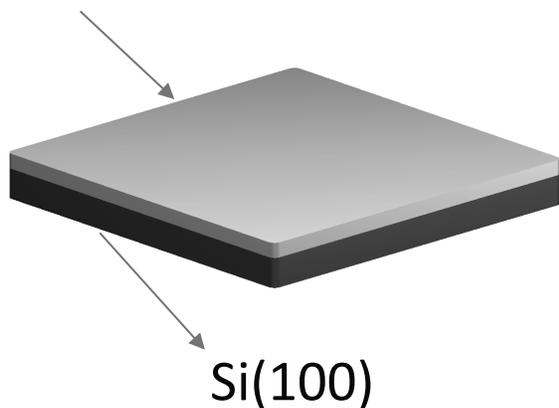


# Sintering resistant Au sub-nanocatalyst



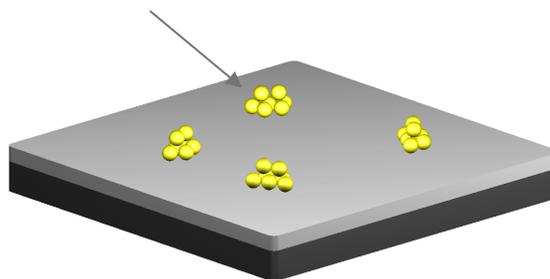
# Sintering resistant Au sub-nanocatalyst

ALD alumina



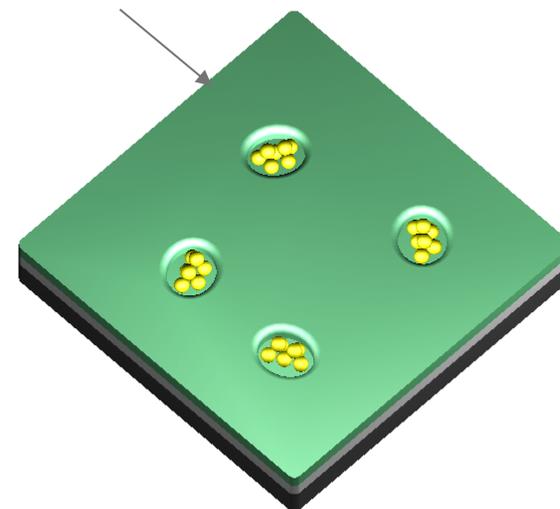
3ML alumina film  
by atomic layer  
deposition (ALD)

Au nanocluster



$Au_{6-10}$  clusters  
soft-landed on  
the alumina film

ALD alumina overcoat

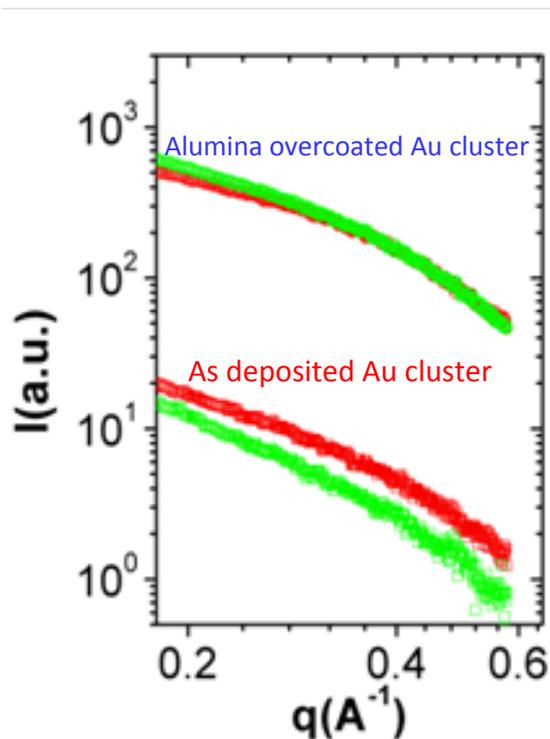


2ML additional ALD  
alumina layer was  
grown selectively



# Stabilization of supported nanoparticles by selective ALD-oxide overcoating

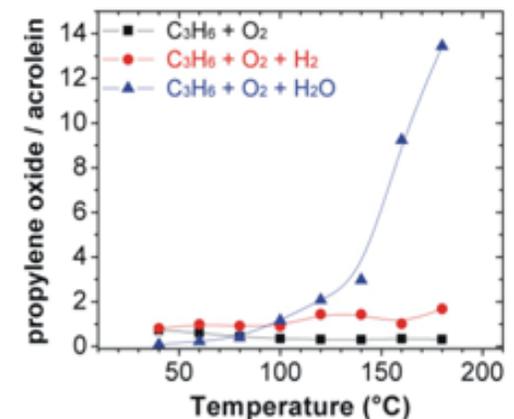
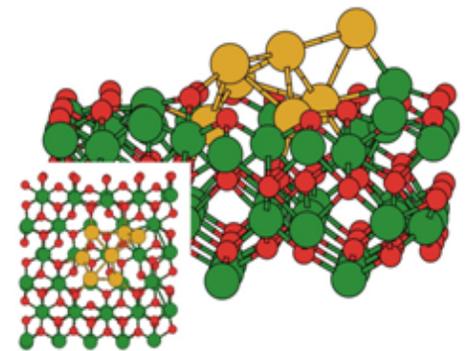
- Selected propene epoxidation on Immobilized Au<sub>6-10</sub> clusters



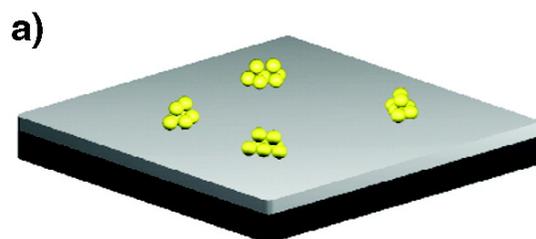
**Green Circles** - data before the heat treatment in the presence of propylene and oxygen

**Red circles** - data taken after the several hours long treatment reaching 300 °C and cooled back to room temperature.

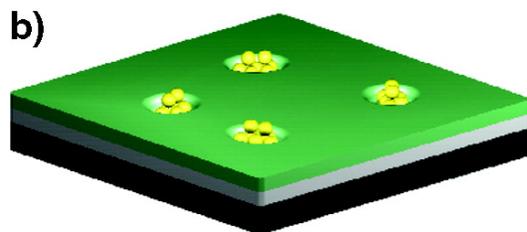
For clarity, the intensity of the scattering from as-deposited clusters was scaled down by a factor of 10.



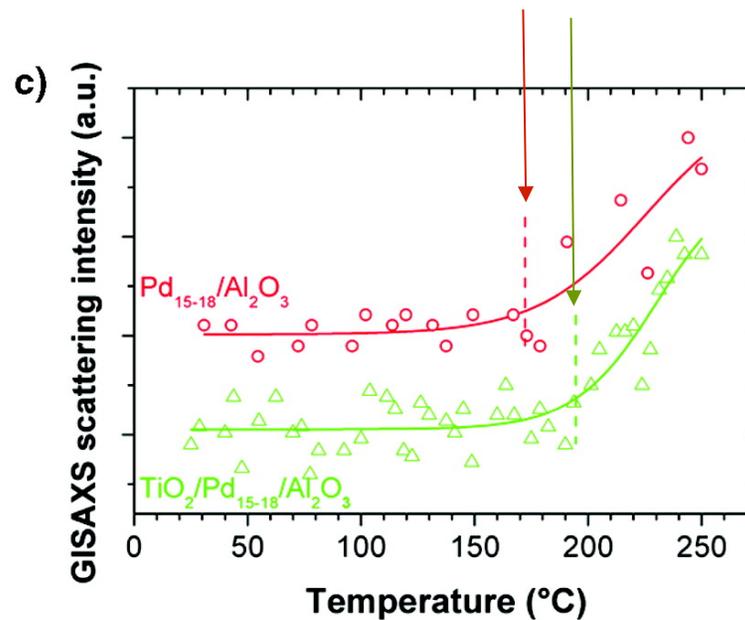
# Stabilizing Pd on Al<sub>2</sub>O<sub>3</sub> with Overcoating by TiO<sub>2</sub>



Cluster sample Pd<sub>15-18</sub>/Al<sub>2</sub>O<sub>3</sub>



Titania overcoated cluster sample  
TiO<sub>2</sub>/Pd<sub>15-18</sub>/Al<sub>2</sub>O<sub>3</sub>

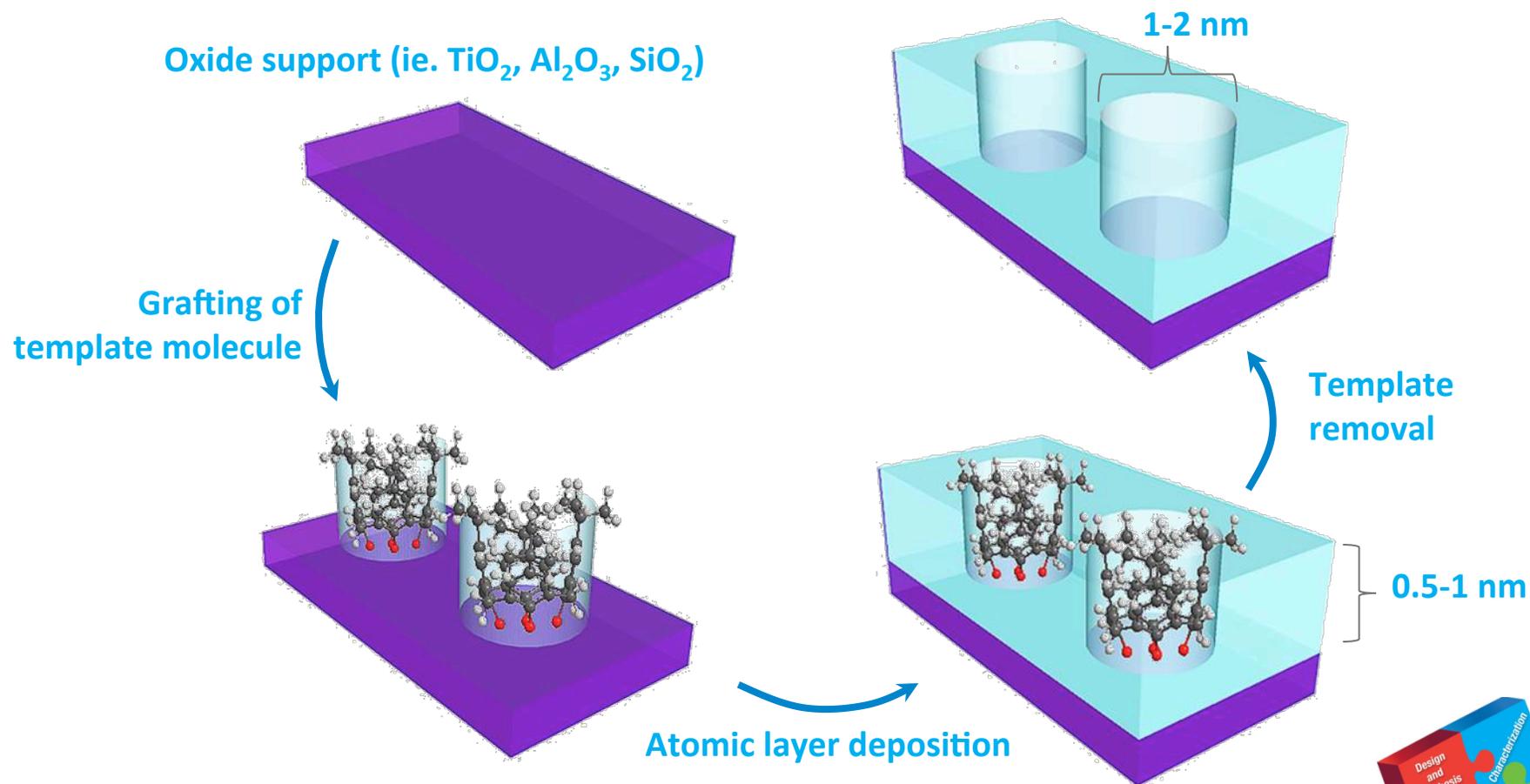


# Summary

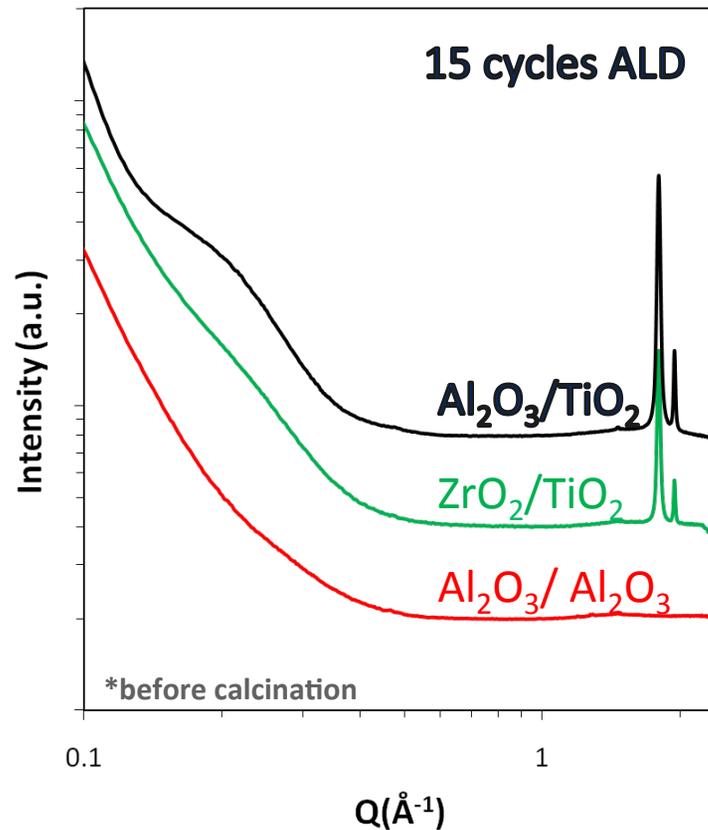
- Demonstration of the powerful combination of cluster deposition, support preparation and X-ray techniques, that can aid the design of new nanoparticle-support combinations.
- Contribution to the understanding size & shape effects in catalysis and catalysis at molecular level
- Catalyst shape changes upon the exposure to the reactant gas mixture at room temperature
- Complex evolution of particle shape with temperature
- Reactivity and selectivity towards propylene oxide strongly depends on catalyst size



# Synthesis of Nanobowls Using Molecular Templates



# Nanobowl: analysis by SAXS

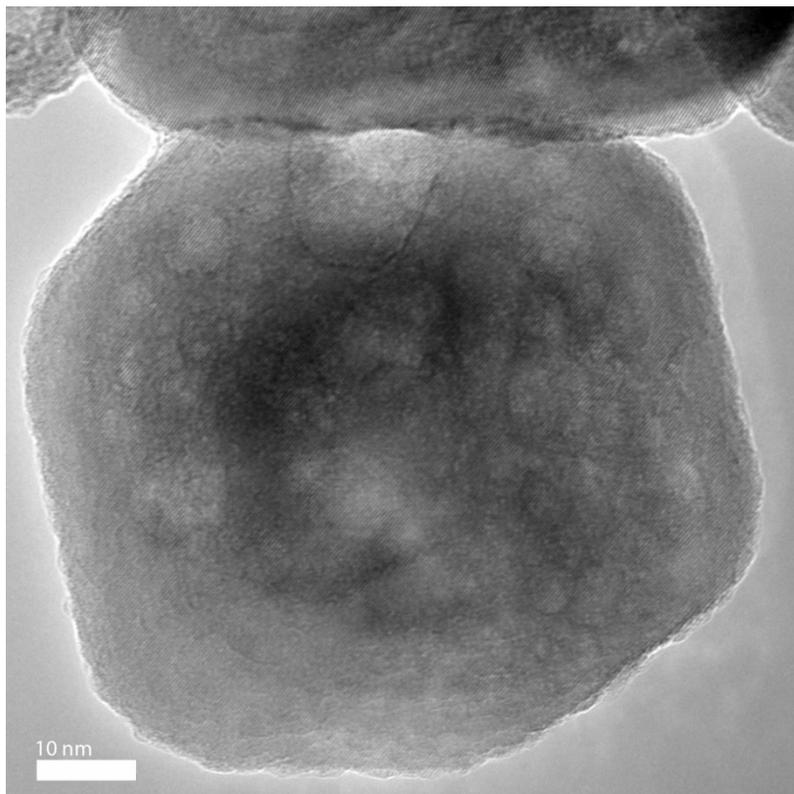


- Screening for best combination of oxides pair for synthesis ( $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{ZrO}_2$ ,  $\text{Al}_2\text{O}_3$ )
- Provide critical information in early stage of project
- Minimize trial and error

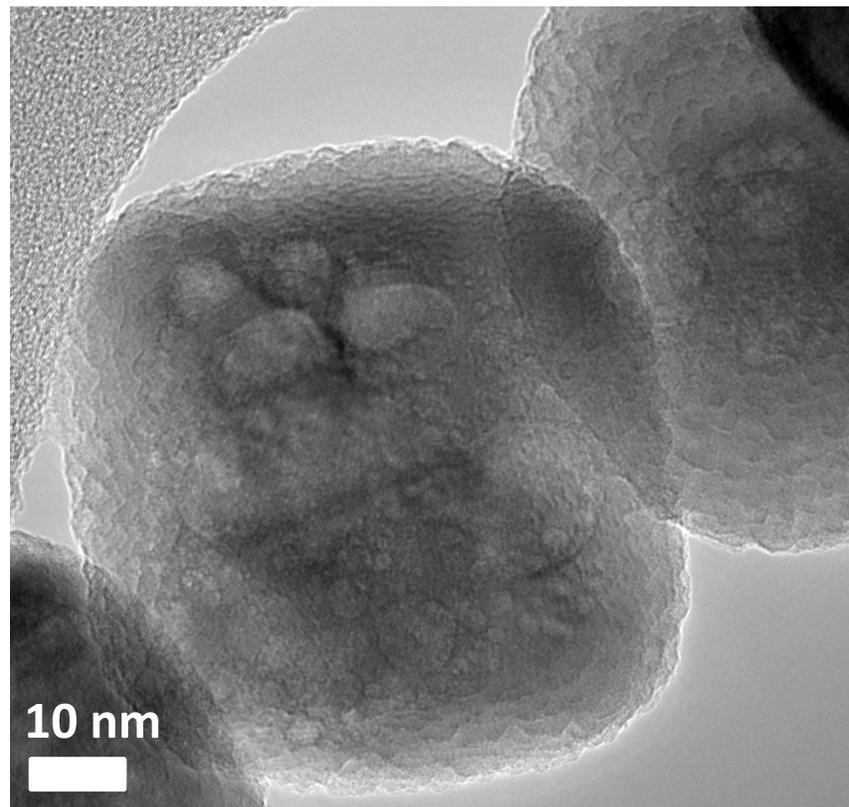


# Observe pitted surfaces

10 cycles  $\text{Al}_2\text{O}_3$  on  $\text{SrTiO}_3$  - no template

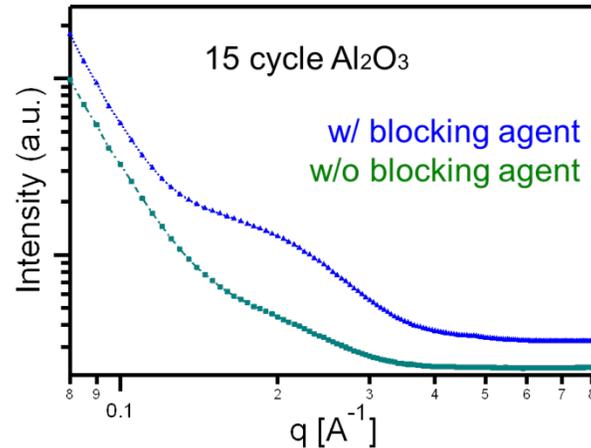
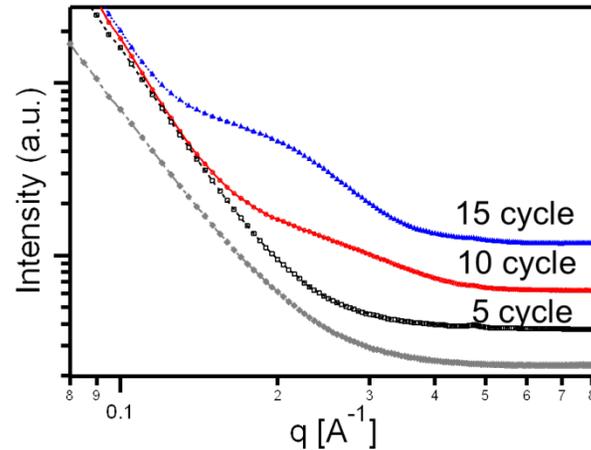
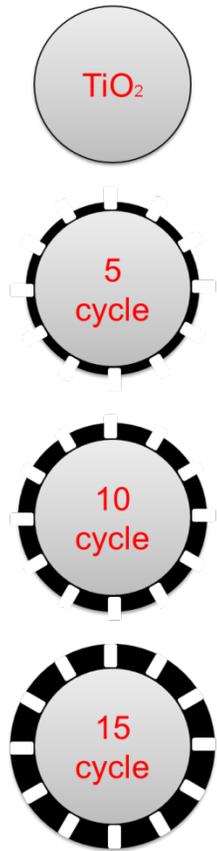


10 cycles  $\text{Al}_2\text{O}_3$  on calix- $\text{SrTiO}_3$



# Nanobowl: analysis by SAXS

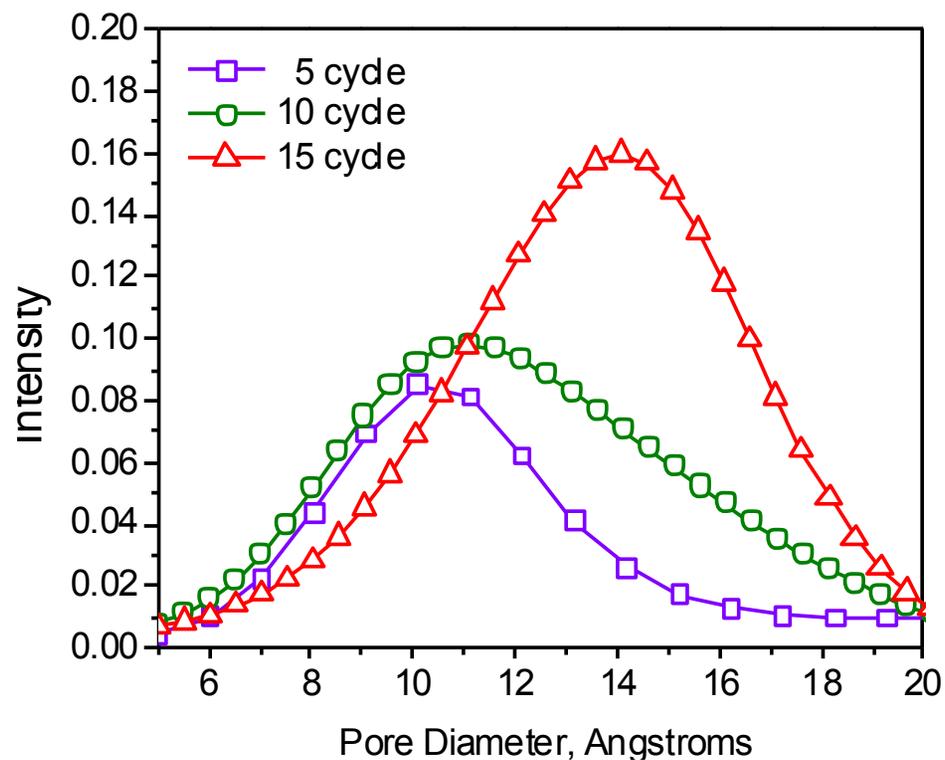
$\text{Al}_2\text{O}_3/\text{calixarene}/\text{TiO}_2$



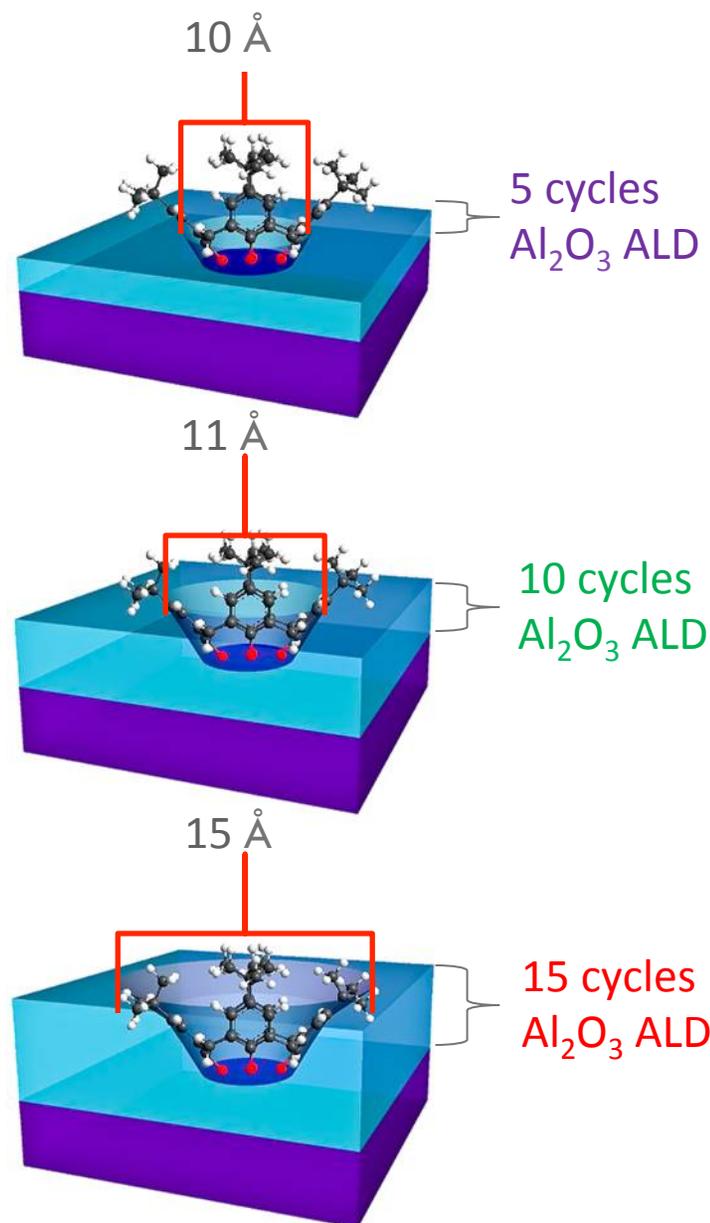
- Layer by layer growth of alumina form cylindrical cavities on TiO<sub>2</sub> nanoparticles.
- SAXS data clearly show the evolution of nanostructure which cannot be clearly identified by electron microscopy techniques.



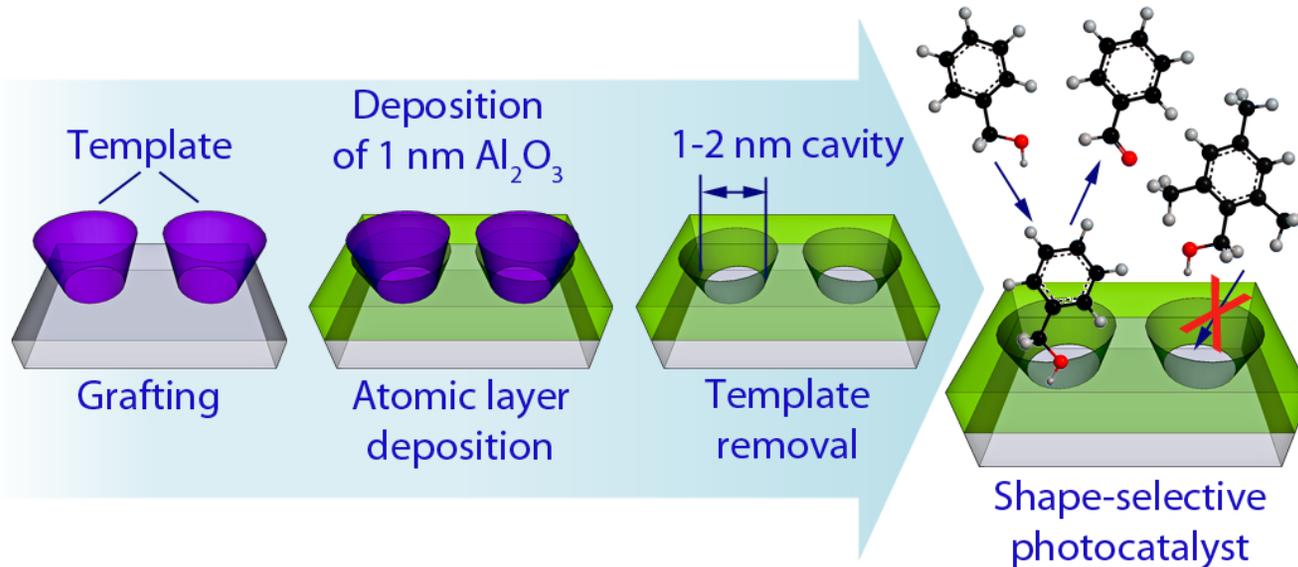
# Small Angle X-ray Scattering



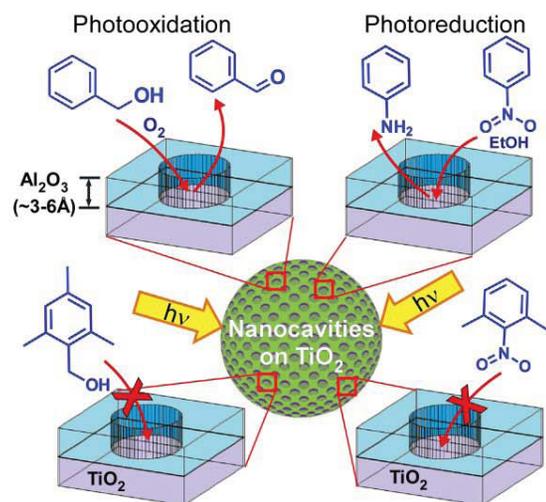
SAXS data fitting results are well matched with the molecular geometry of the blocking agent.



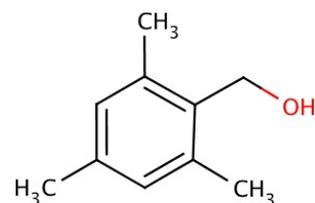
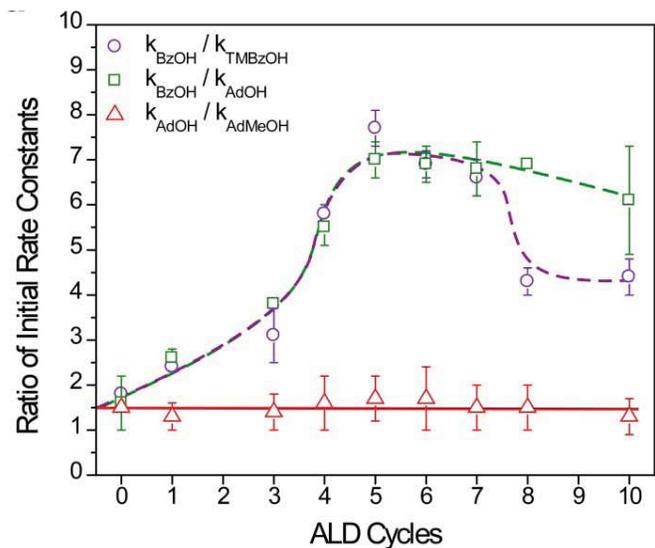
# Nanobowl: molecular level reaction control shape selective catalyst



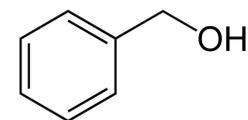
# Nanobowl: molecular level reaction control by shape selective catalyst



Selectivity of photo catalytic reaction strongly depends on steric effect and shape of reactants molecule.



Trimethylbenzyl alcohol (TMBzOH)



Benzyl alcohol (BzOH)

## Conclusion

- Small nanoparticles are important for various applications: nano-catalyst, quantum dot
- Dynamic change occurs at high temperature and reactive gas environment
- A series of SAXS based studies successfully identifies a problem and provides a key step to develop a new type of advanced catalytic material
- Nanobowl is one successful approach to control reactions by molecular scale architecture



# Ordered liquid crystalline phase to nanocrystalline nanocube ( $\text{SrTiO}_3$ nanocubes) formation

Sungsik Lee and Randall Winans XSD

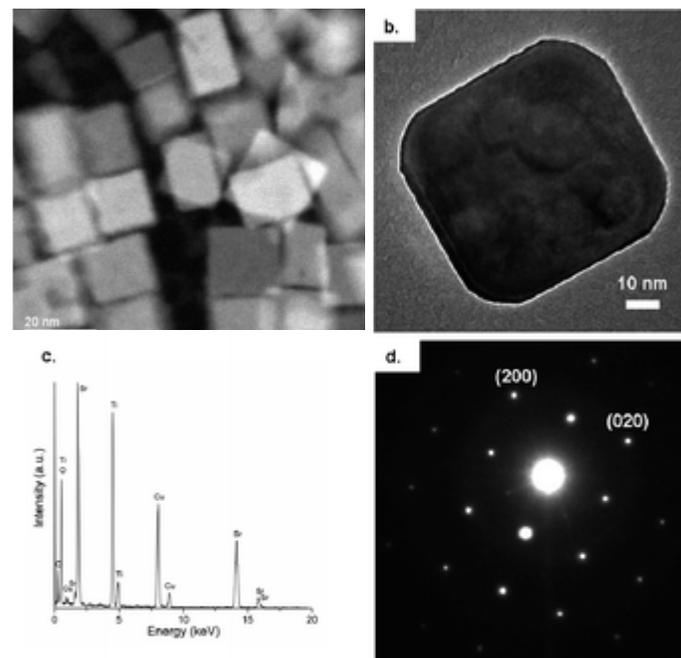
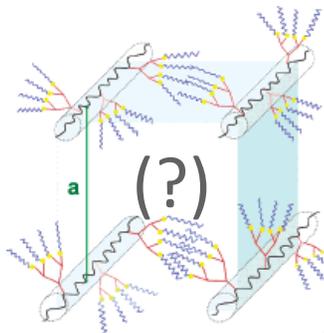
Linhua Hu and Ken Poeppelmeier, Northwestern U



Not much information on initial or intermediate stage during the hydrothermal reaction (at high temperature and pressure condition)

$\text{Ti}(\text{OBU})_4$   
Ethanol  
Oleic Acid  
 $\text{Sr}(\text{Ac})_2$   
 $\text{NaOH}(\text{aq})$

160-210 °C, 5 atm, 8 ~24 hours



# In-situ SAXS/WAXS setup

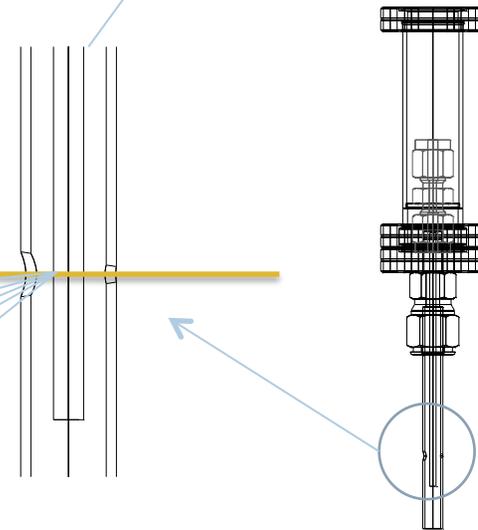
Liquid crystalline phase formation and change  
1 nm to 100 nm range order



12KeV X-ray

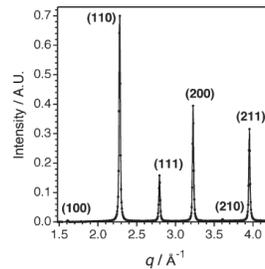


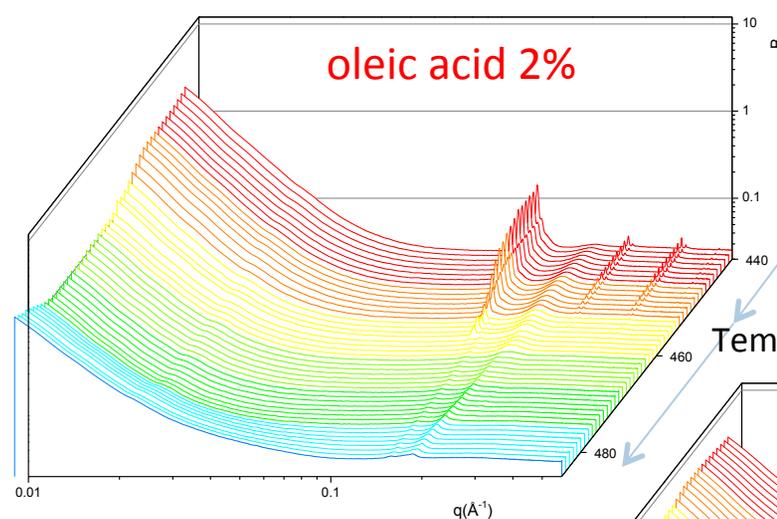
Quartz capillary



Pressure > 150 psi

Solid nanocube formation  
Crystalline structure of STO  
High temperature curing  
Å range order

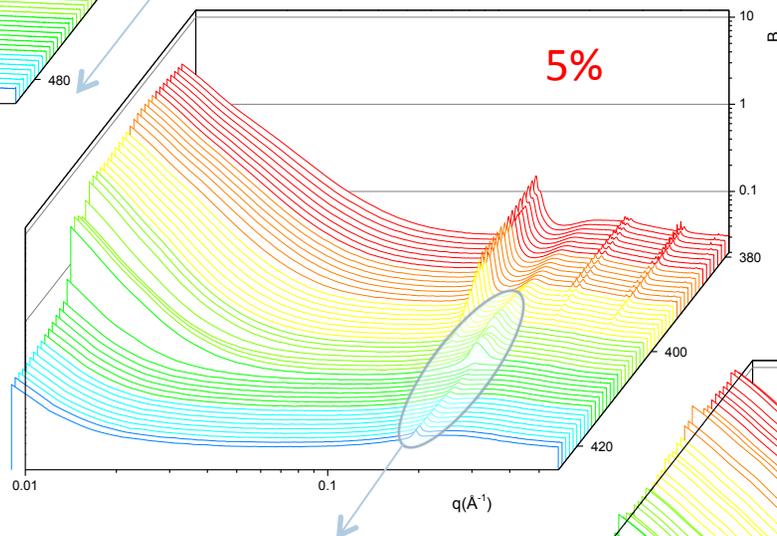




oleic acid 2%

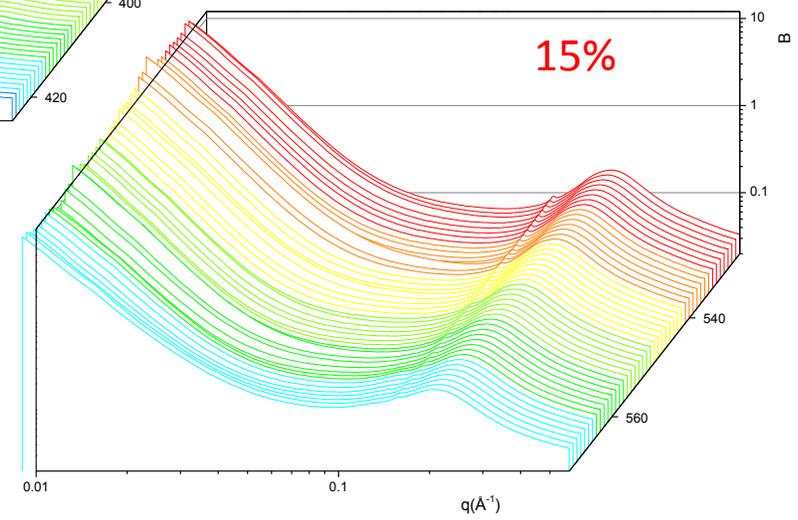
Irregular  
round nanoparticle

RT time every 30 sec in 5 min.  
Temperature ramp up to 160 °C



5%

well-defined structure  
even at high temperature  
regular nanocuboid

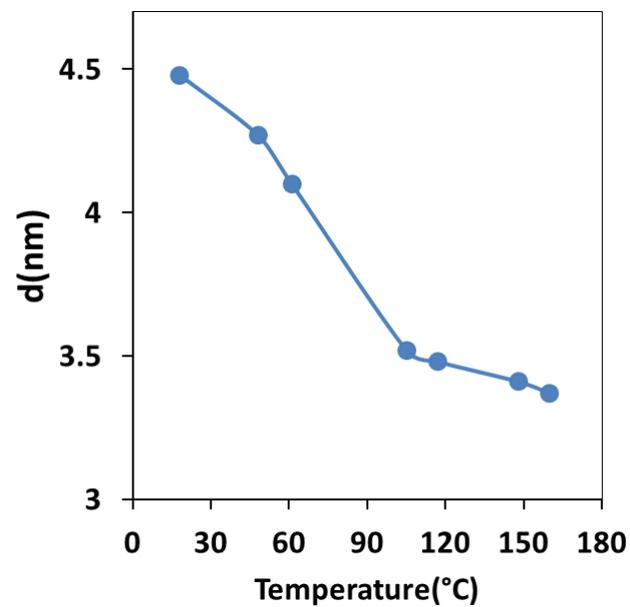
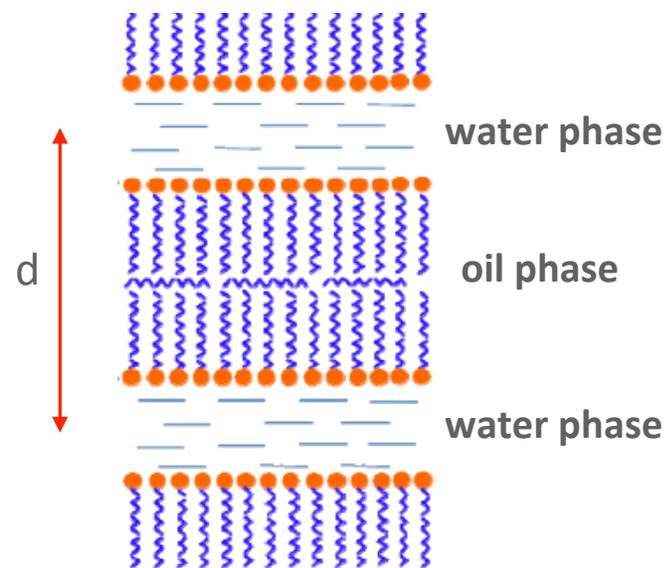
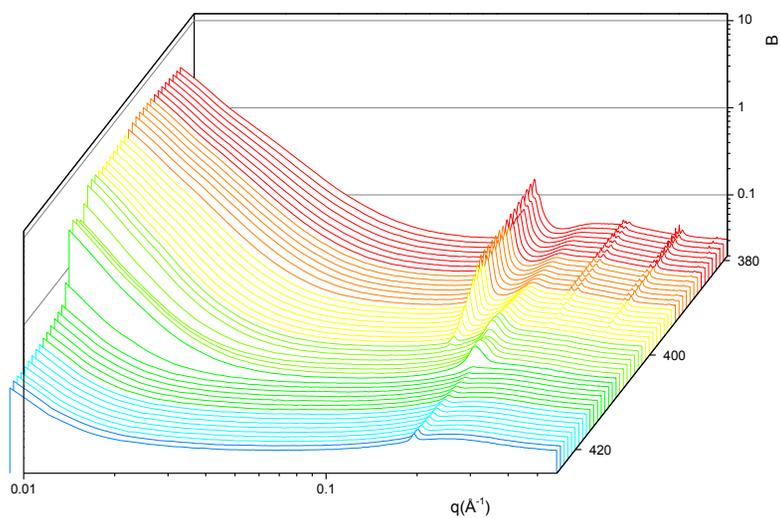
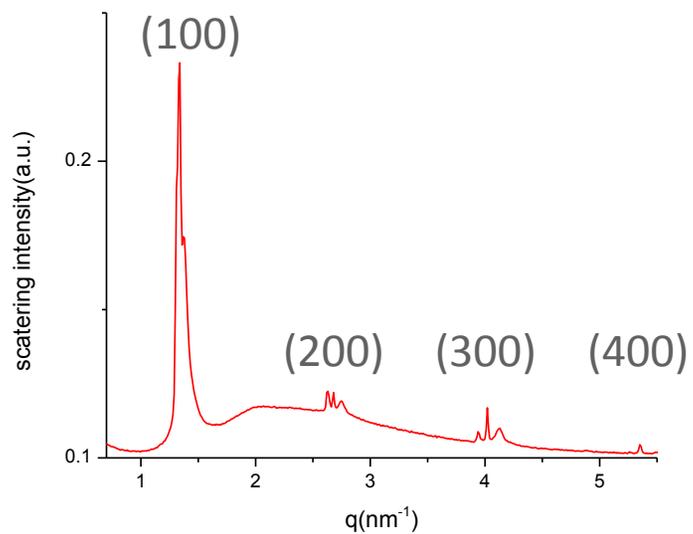


15%

round nanorods



## 5 % : oleic acid



# Conclusions

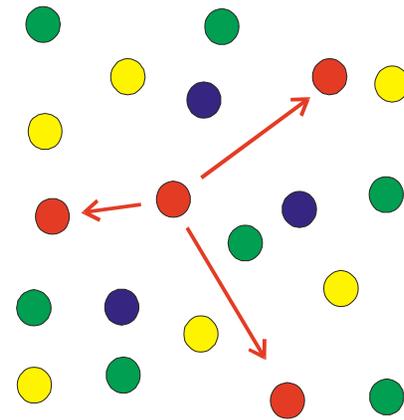
- In-situ SAXS and WAXS analysis confirms the lamellar liquid crystal structure of  $\text{SrTiO}_3$  in hydrothermal reaction condition
- Different concentration of oleic acid will lead to final morphology of nanoparticles
- Lamellar structure confirmed by SAXS is the key factor during hydrothermal synthesis from the nuclei to nanocuboids



# Anomalous Small Angle X-ray Scattering (ASAXS)

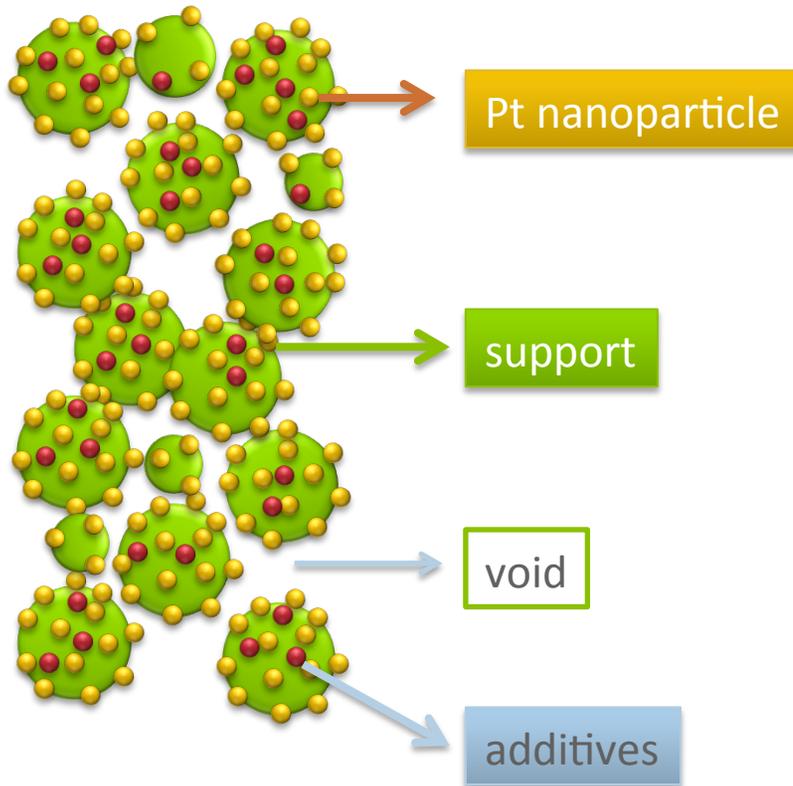
## What is ASAXS?

*Anomalous small angle X-ray scattering* (ASAXS) refers to extensions of standard SAXS experiments in which the energy of the probing X-rays are tuned *near the absorption edge* of an element in the sample. By performing SAXS experiments near the characteristic absorption edge of any given atom, it is possible to vary the contrast for scattering of that *particular element*.



# Anomalous Small Angle X-ray Scattering (ASAXS)

- Supported Pt catalyst



SAXS Problem:  
difficult to interpret  
*“complex system” !!*

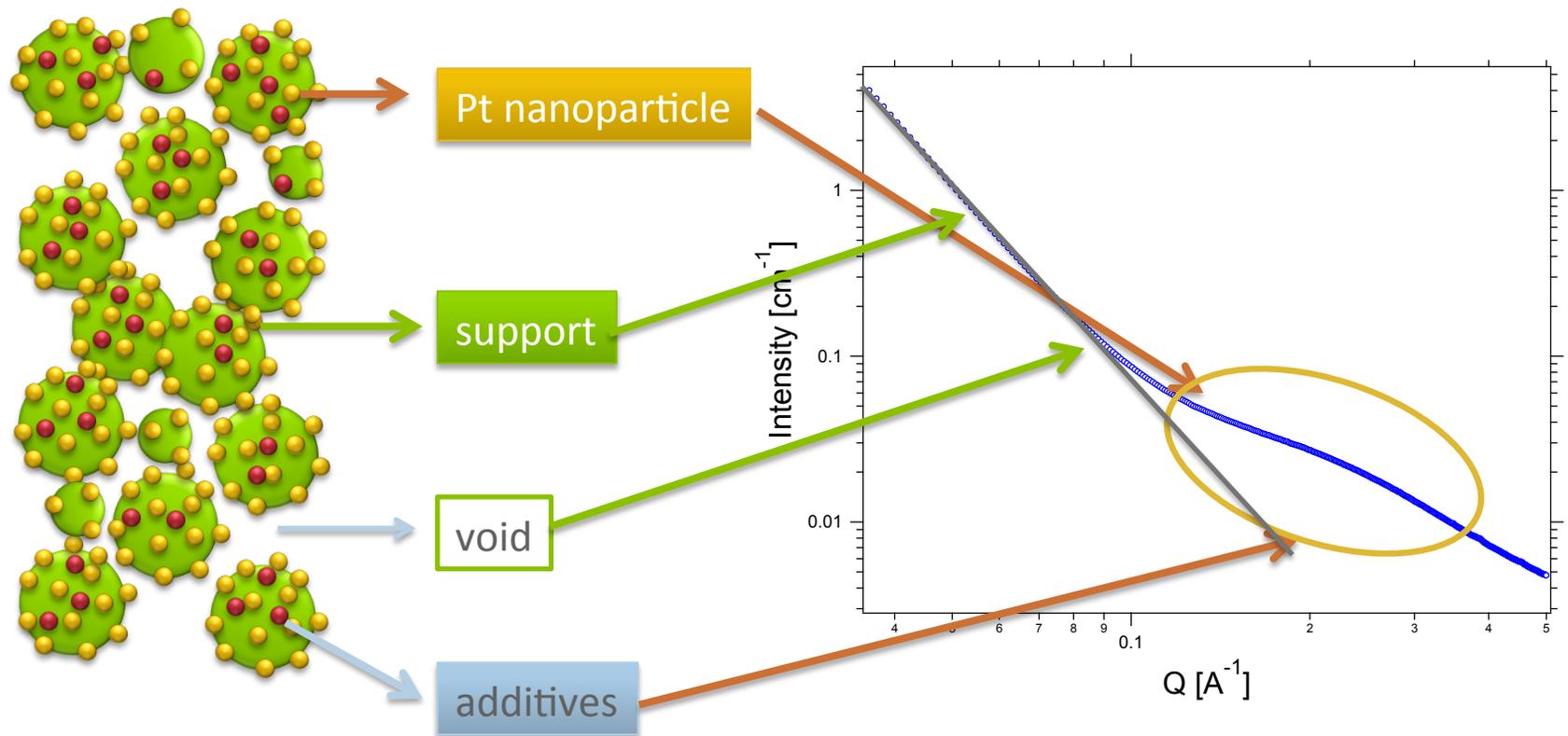
Scattering from

- Pt nanoparticles
- Inhomogeneous support
- Porous media
- Additives



# Anomalous Small Angle X-ray Scattering (ASAXS)

- Supported Pt catalyst



# Anomalous Small Angle X-ray Scattering (ASAXS)

- Scattering intensity

$$\frac{d\Sigma}{d\Omega}(Q) = c_0(n_p f_p - n_m f_m)^2 S^2(Q) V^2 + \frac{d\Sigma}{d\Omega_{bg}}(Q)$$

$n_p, n_m$ : number density

$f_p, f_m$ : atomic form factor

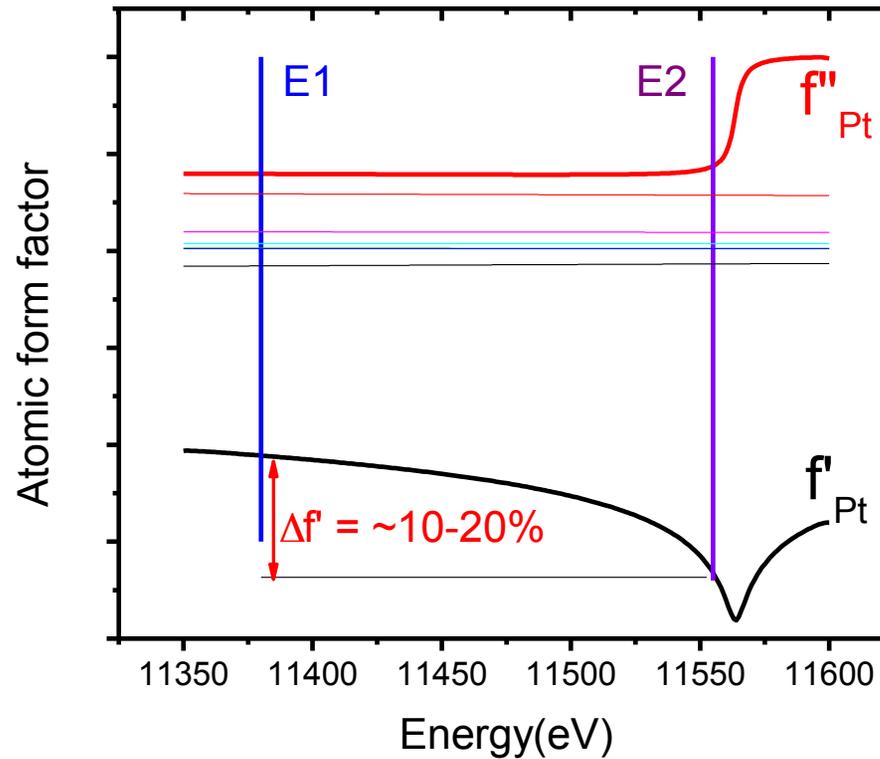
$S(Q)$ : particle form factor

$$\underline{f(E) = f_0 + f'(E) + if''(E)}$$

*Energy dependent*



# Anomalous Small Angle X-ray Scattering (ASAXS)



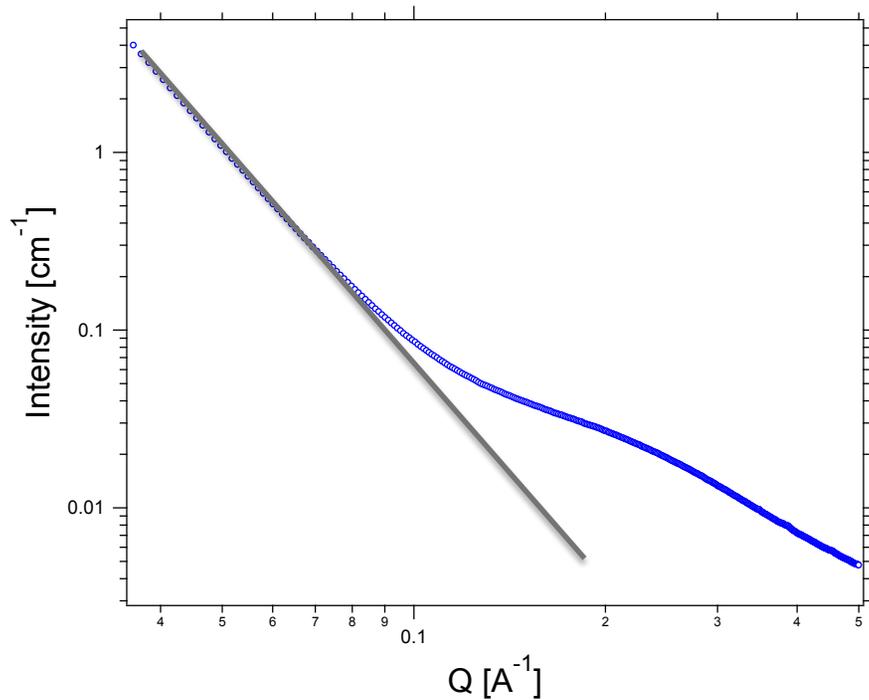
$f(E) = f_0 + f'(E) + if''(E)$ : atomic form factor

$$\frac{d\Sigma}{d\Omega}(Q)_{Pt} = \frac{d\Sigma}{d\Omega}(Q, E_1) - \frac{d\Sigma}{d\Omega}(Q, E_2)$$

**Element sensitive contrast**



# TiO<sub>2</sub>/Pt/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ASAXS



To analyze this  $I(q)$  from SAXS,  
Unified fit or model fit to find the  
best fit.

Assumption!!

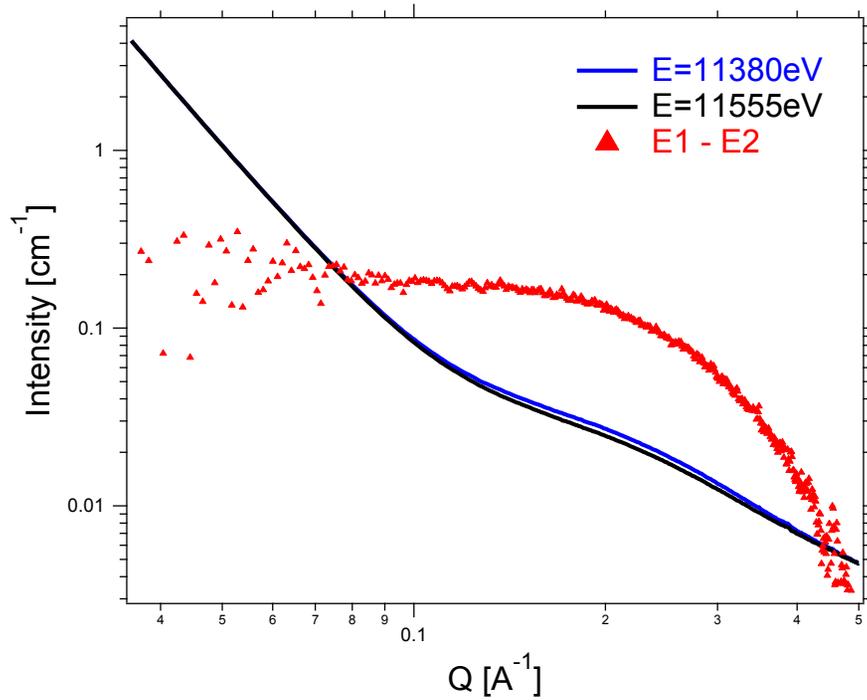
*Best fit = right solution*

*All changes during the in-situ reaction :  
result from the element of interest*

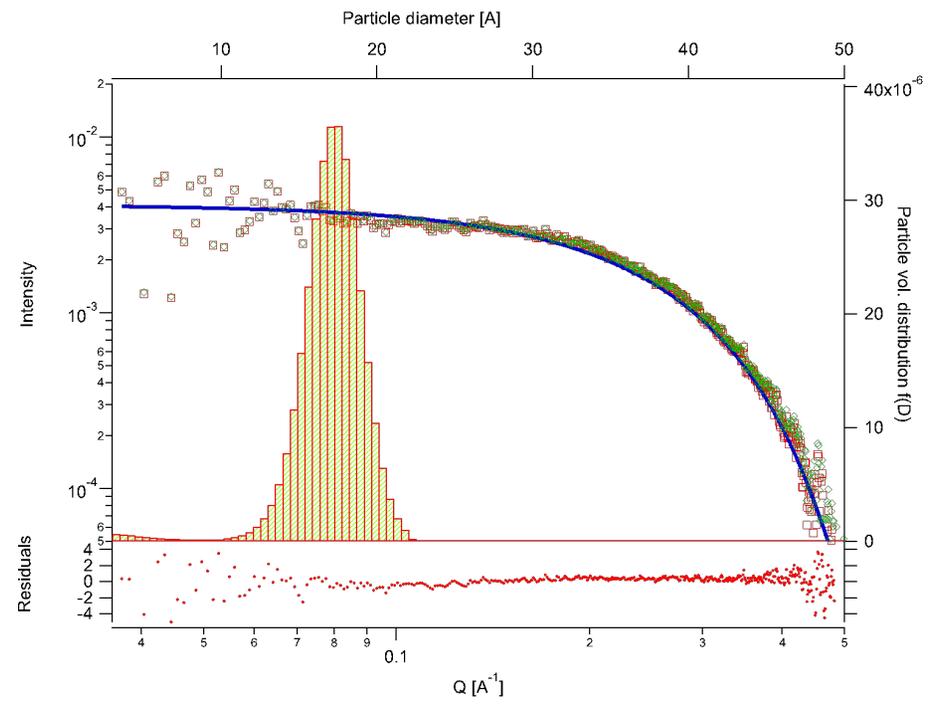
*NOT ALWAYS TRUE*



# TiO<sub>2</sub>/Pt/TiO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> ASAXS

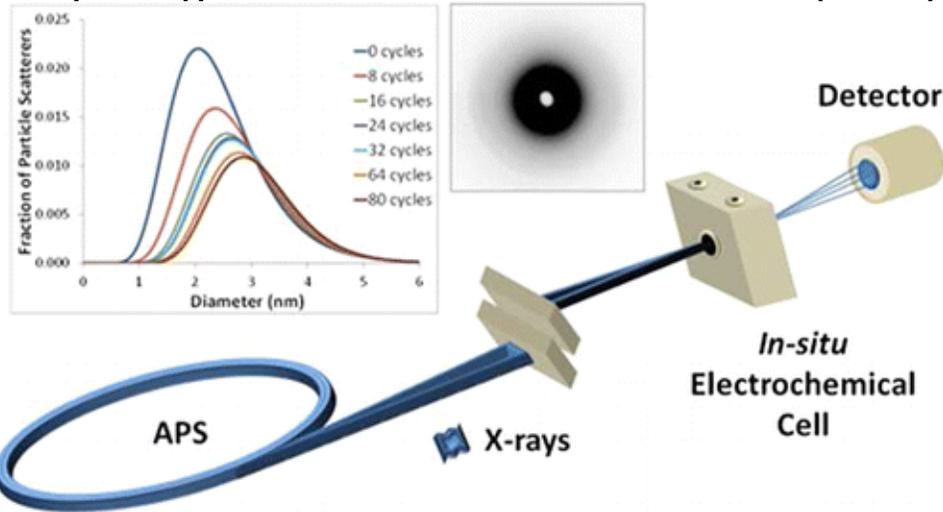


- Difference spectra : signal only from the **Pt nanoparticles**
- Exclude possible Ti particles or support contribution



# ASAXS: examples

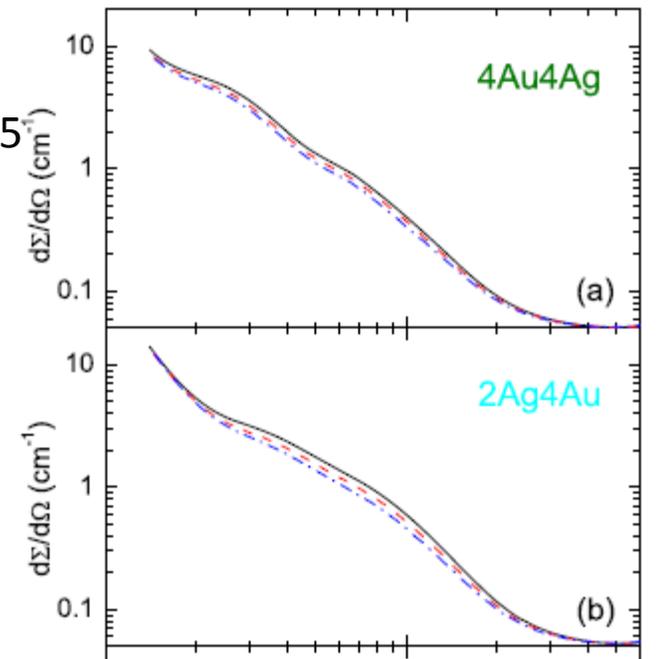
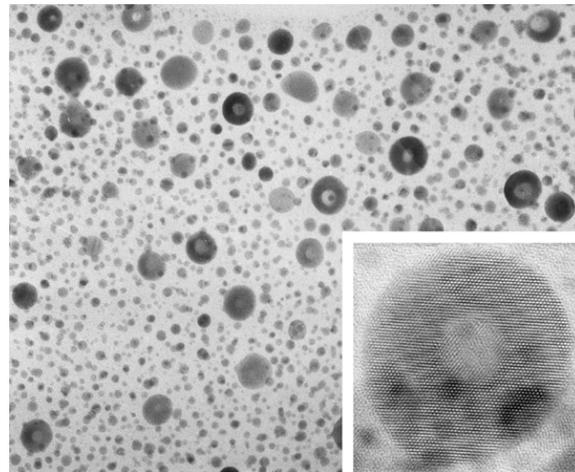
In situ anomalous small-angle X-ray scattering studies of platinum nanoparticle fuel cell electrocatalyst degradation. *J. Am. Chem. Soc.* 134(2012) 14823



**Complex system:  
electrolytes, carbon based  
support in-situ reaction  
condition**

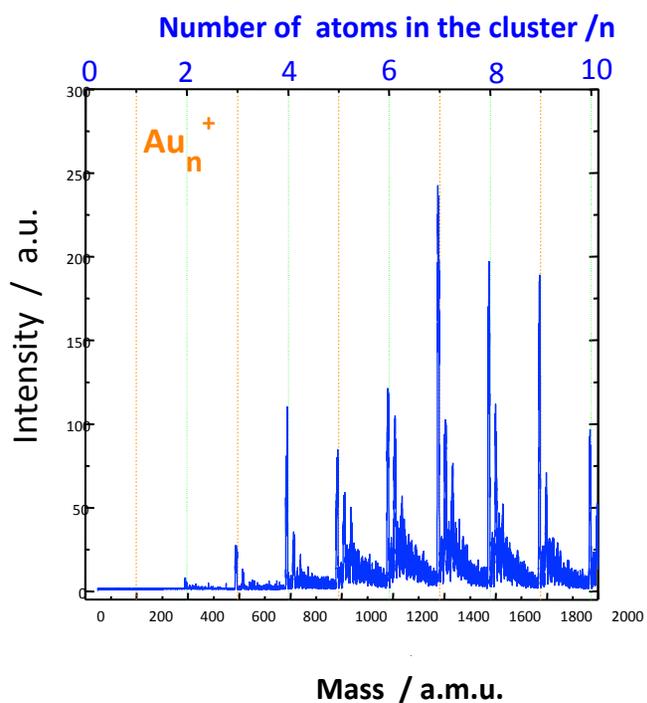
- ASAXS study on the formation of core-shell Ag/Au nanoparticles in glass. *Nanotechnology* **20** (2009) 505705

**Complex system:  
Ag-Au core shell particle  
Core-shell thickness  
calculation**

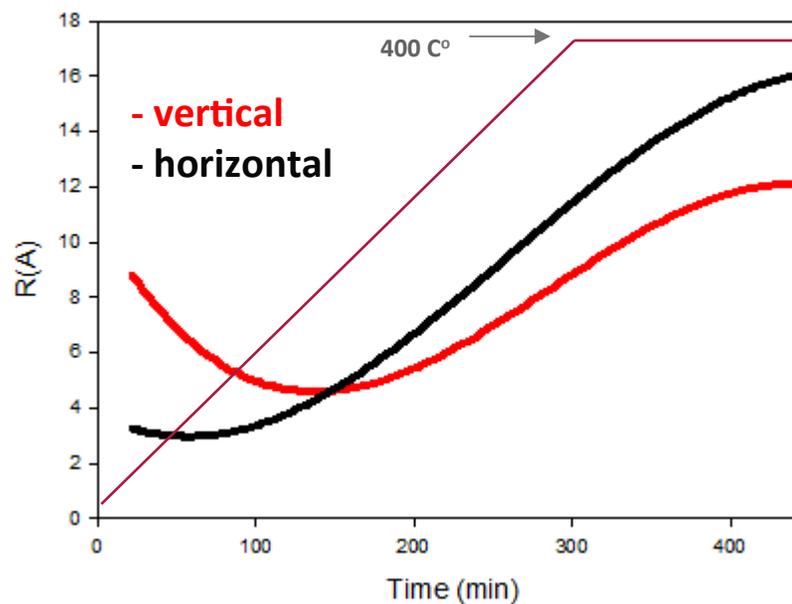


# Size Selected Au Clusters on SiO<sub>2</sub>/Si (111)

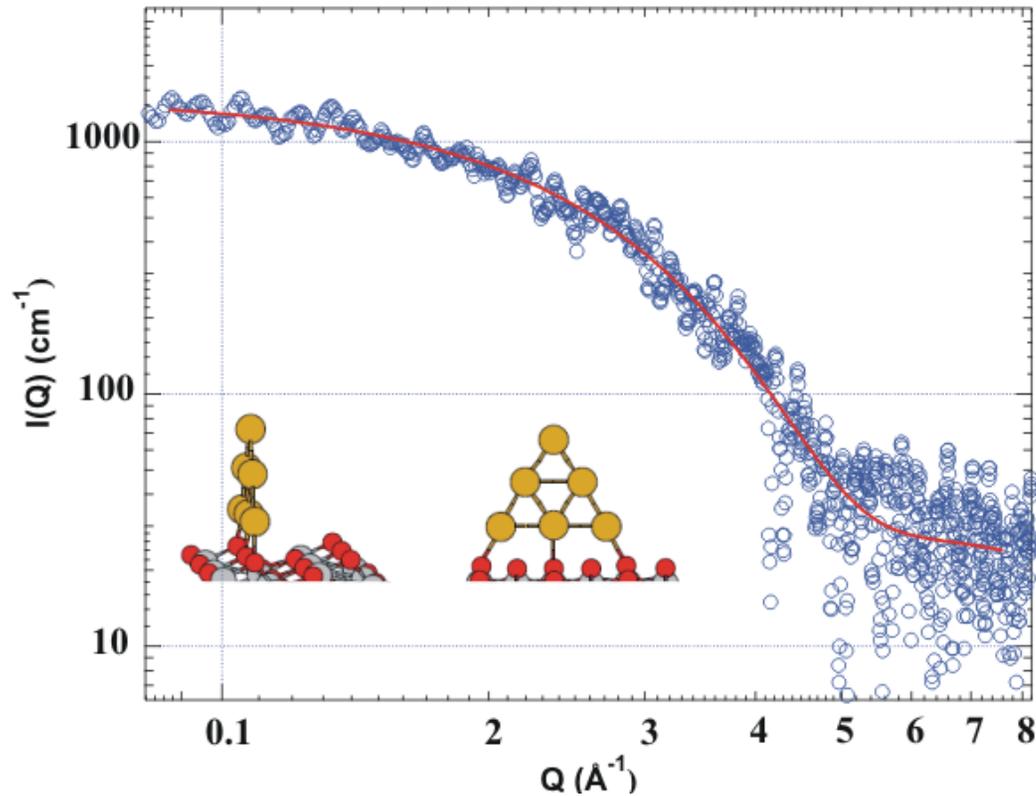
## Effects of H<sub>2</sub>



### Au Clusters with H<sub>2</sub>



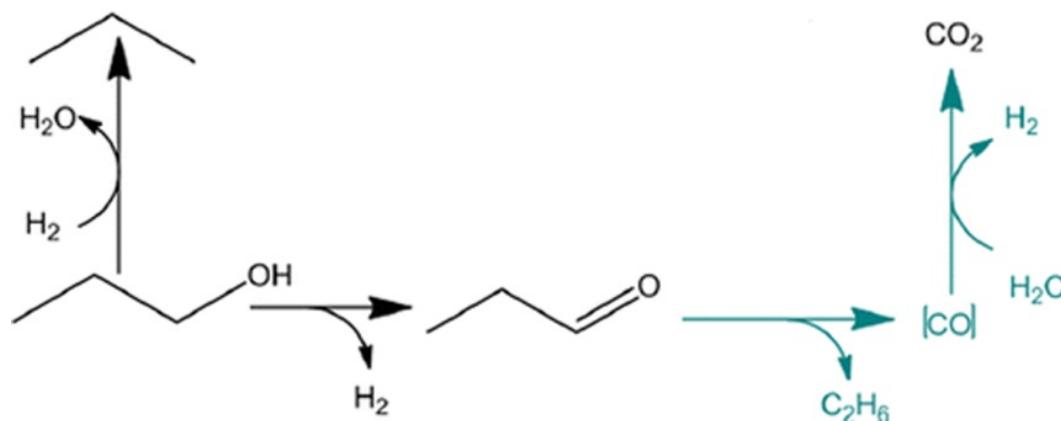
# Anomalous GISAXS Au<sub>6</sub> Clusters



- Dots: experimental AGISAXS signal.
- Line: Simulated GISAXS data for an ensemble of randomly oriented Au<sub>6</sub> discs. Inserted structures courtesy of L. Molina and B. Hammer.

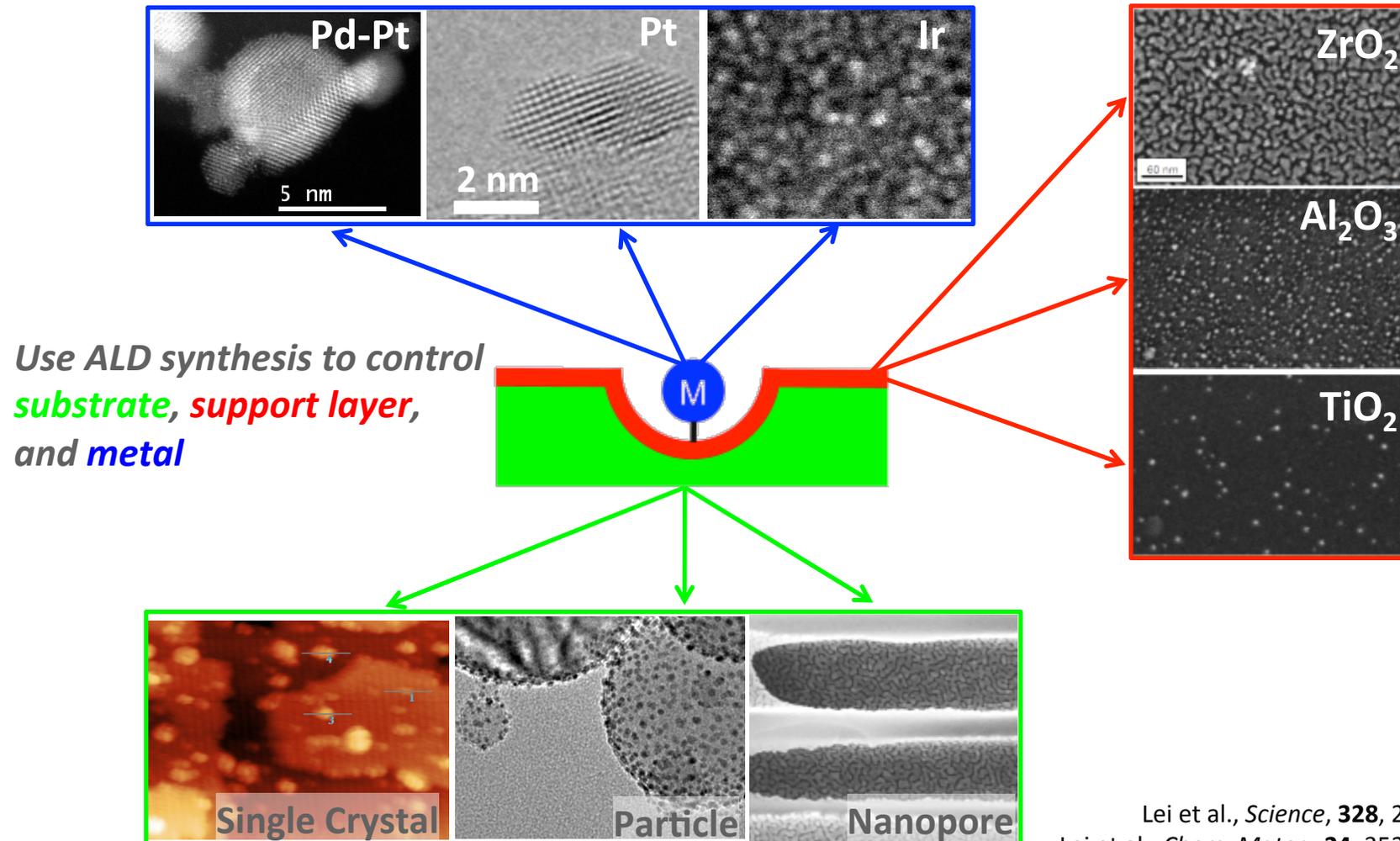


# 1-propanol reforming for H<sub>2</sub>



Propanol is being used as a surrogate for biomass-derived glycerol as a source of hydrogen in the conversion of cellulose to transportation fuels.

# Sample preparation: Atomic Layer Deposition

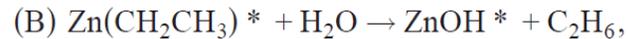
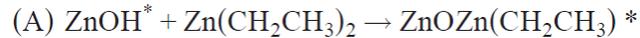


Lei et al., *Science*, **328**, 224-228, 2010  
Lei et al., *Chem. Mater.*, **24**, 3525-3533, 2012  
Lu et al., *Science*, **335**, 1205-1208, 2012  
Christensen et al., *Nano Lett.*, **10**, 3047-3051, 2010  
Elam et al., *MRS Bulletin*, **36**, 899-906, 2011



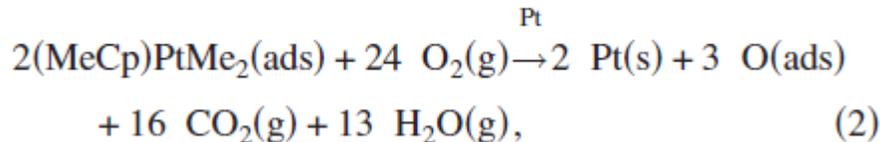
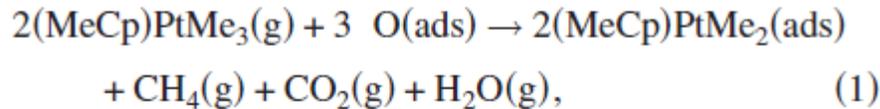
# Sample preparation: Atomic Layer Deposition

## ZnO ALD @ 150 °C



Ferguson *et al.*, *J.Vac. Sci. Technol. A* 23 (2005) 118

## Pt ALD @ 250 °C

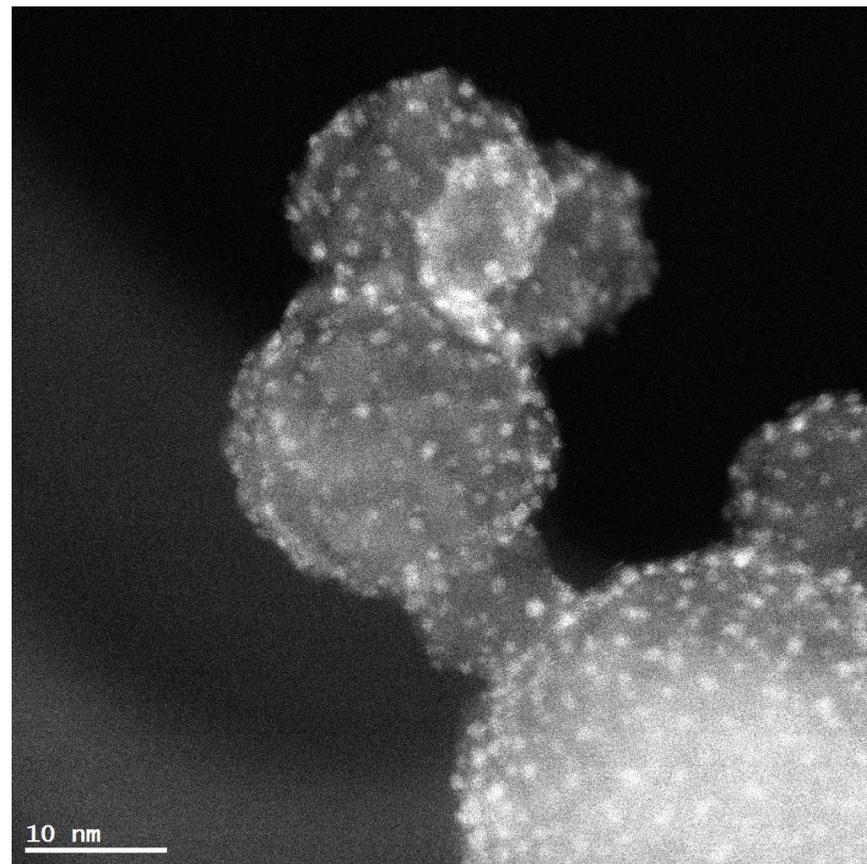
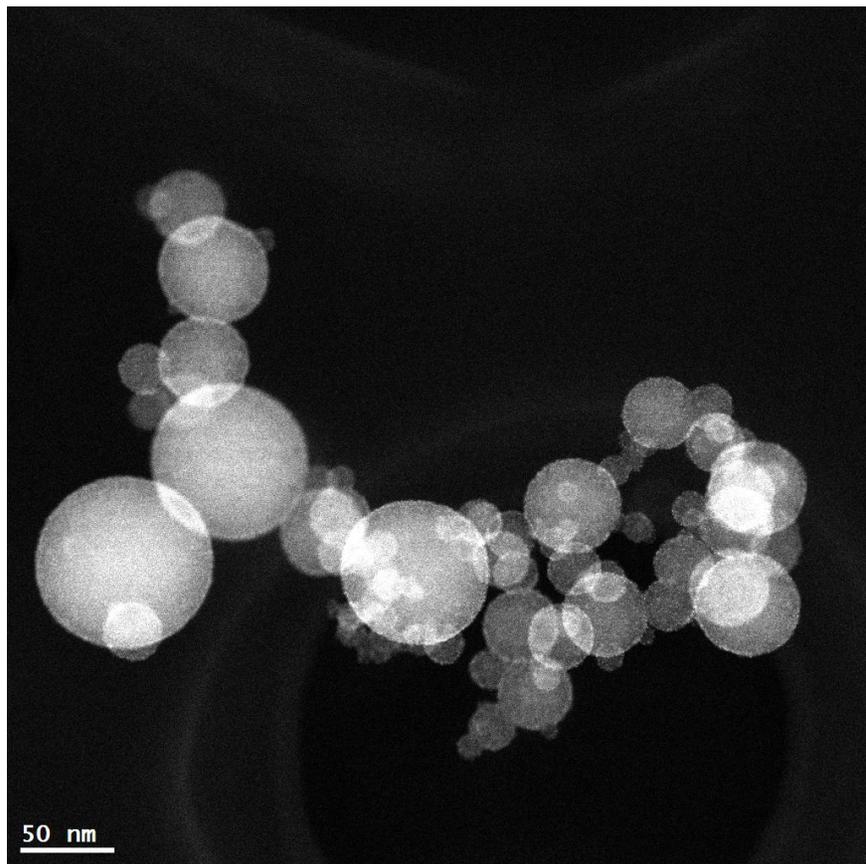


Kessels *et al.*, *Appl. Phys. Lett.*, 95 (2009) 013114

**Pt/Al<sub>2</sub>O<sub>3</sub>   Pt/ZnO/Al<sub>2</sub>O<sub>3</sub>   ZnO/Pt/Al<sub>2</sub>O<sub>3</sub>**



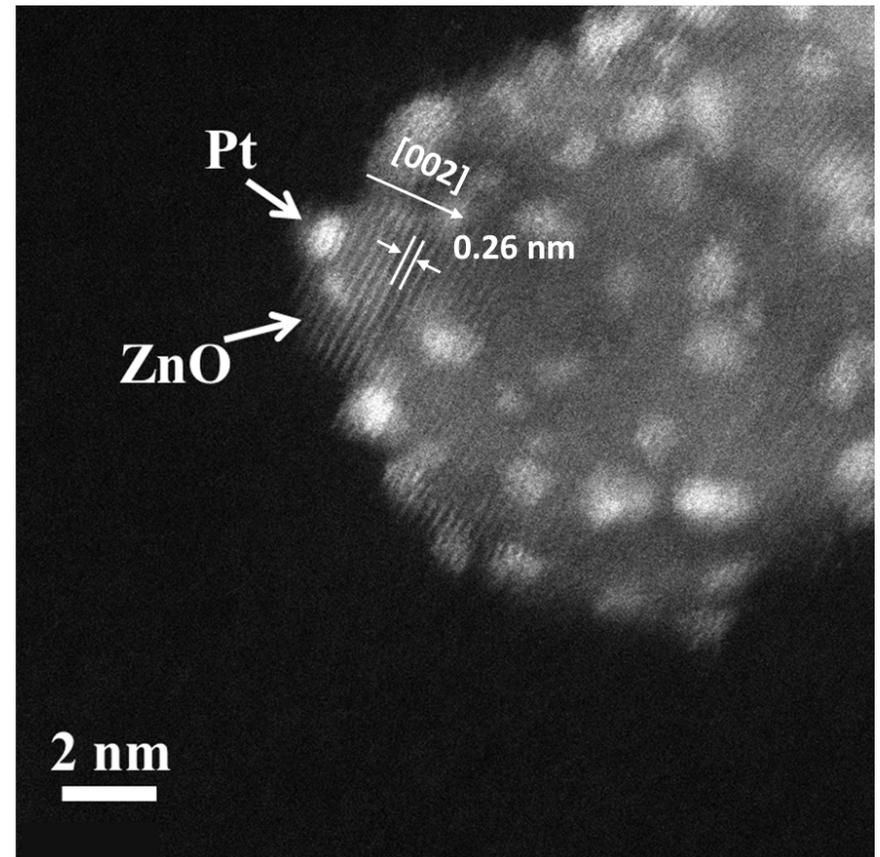
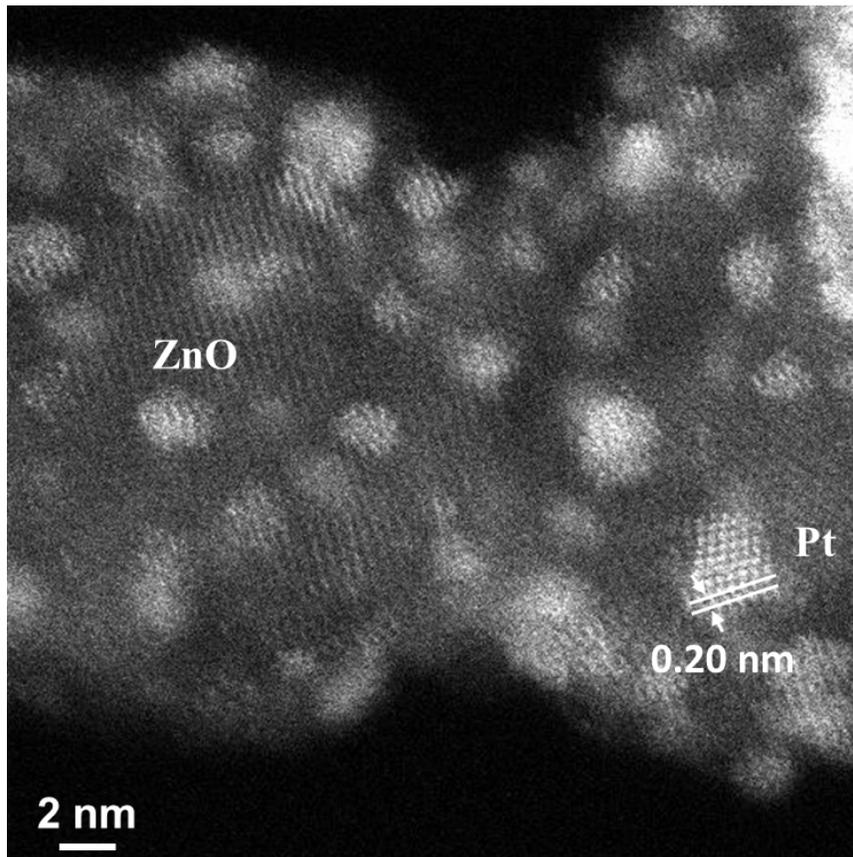
# Pt/ZnO/Al<sub>2</sub>O<sub>3</sub>



Support : ~50 nm size high surface area (30m<sup>2</sup>/g) spherical alumina(NanoDur)



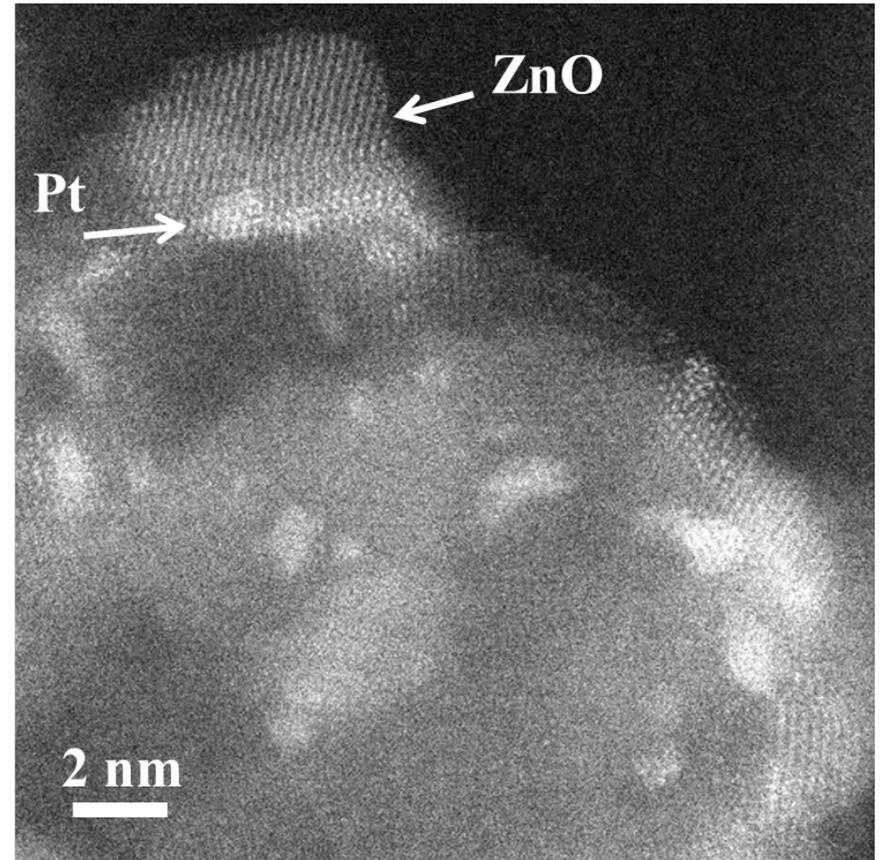
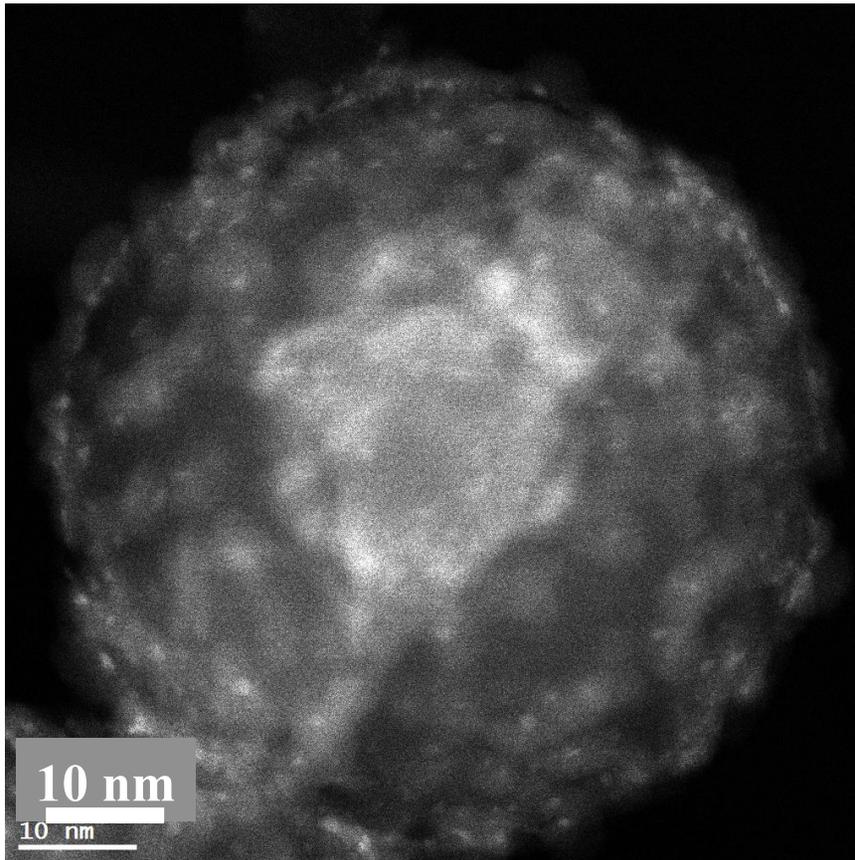
# Pt/ZnO/Al<sub>2</sub>O<sub>3</sub>



- White dots: Pt NPs, 1-2 nm
- Crystalline & Cloud structure: ZnO
- Black: vacuum & Al<sub>2</sub>O<sub>3</sub>



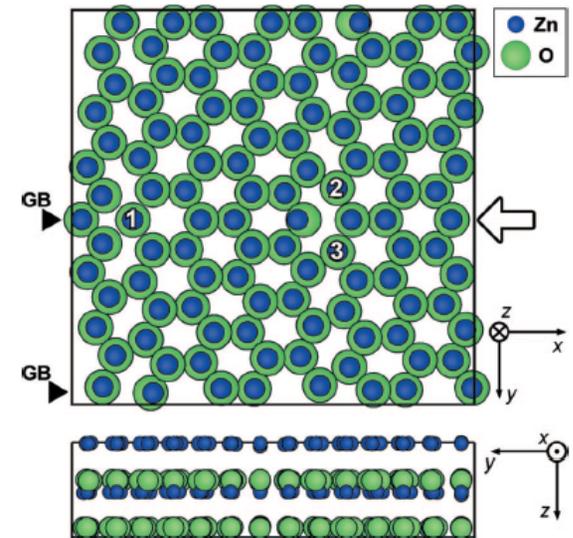
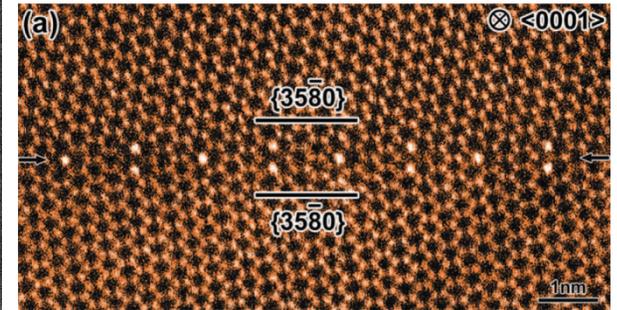
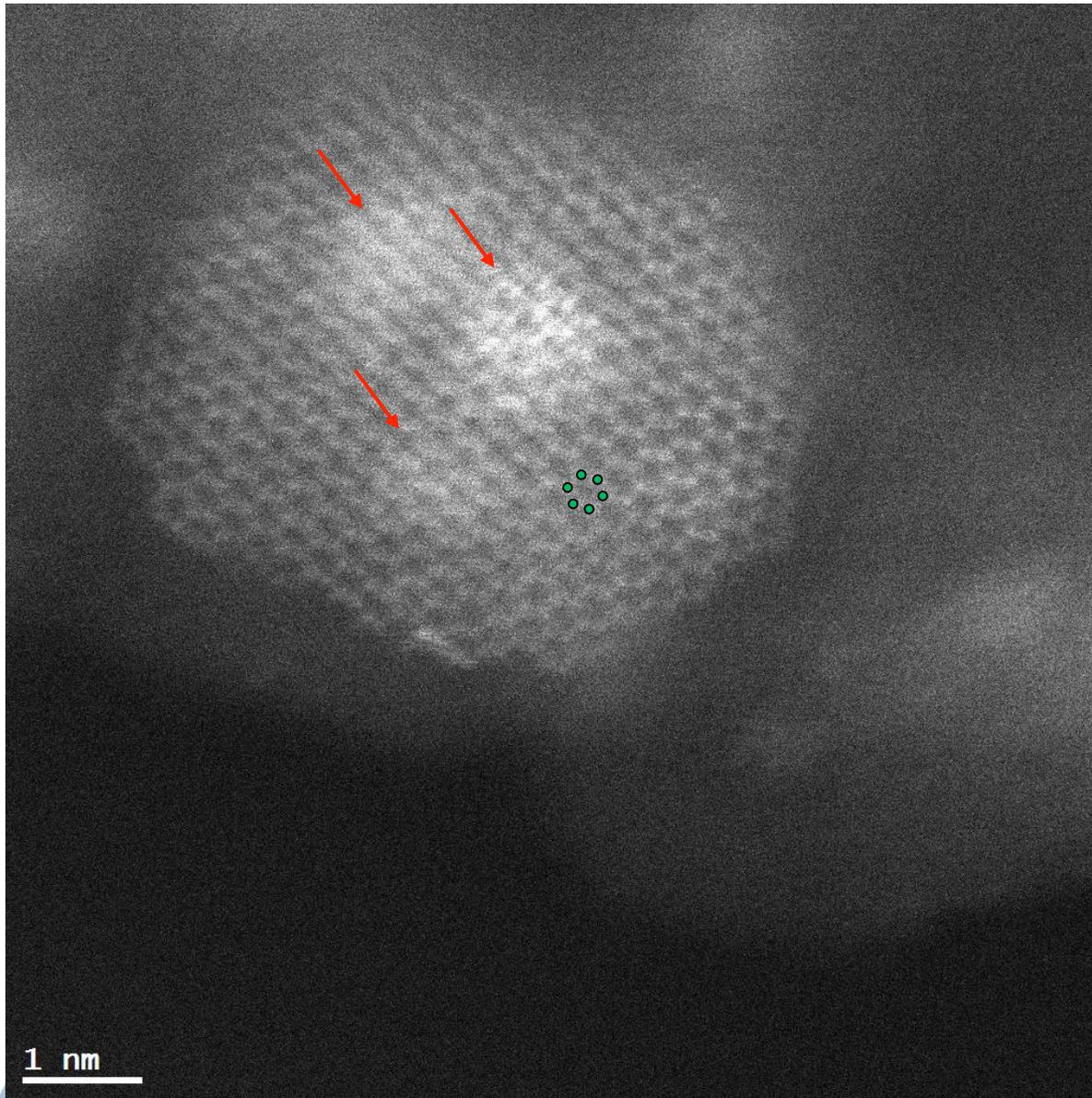
# ZnO/Pt/Al<sub>2</sub>O<sub>3</sub>



- White dot: Pt
- White clode: ZnO
- Black: Vacuum or Al<sub>2</sub>O<sub>3</sub>

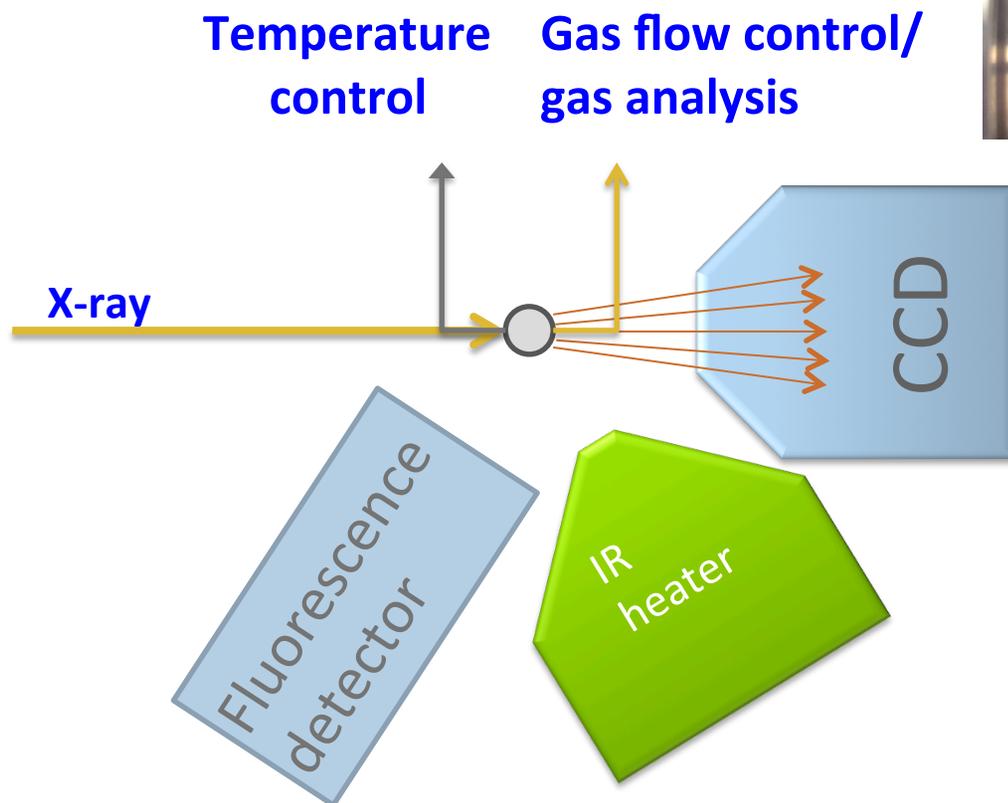
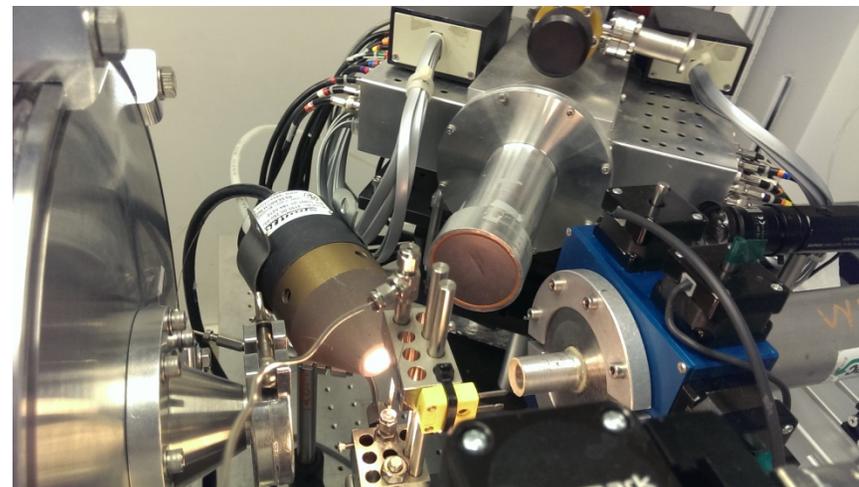


# ZnO/Pt/Al<sub>2</sub>O<sub>3</sub>



Sato et al., *PRB*, 80 (2009) 094114

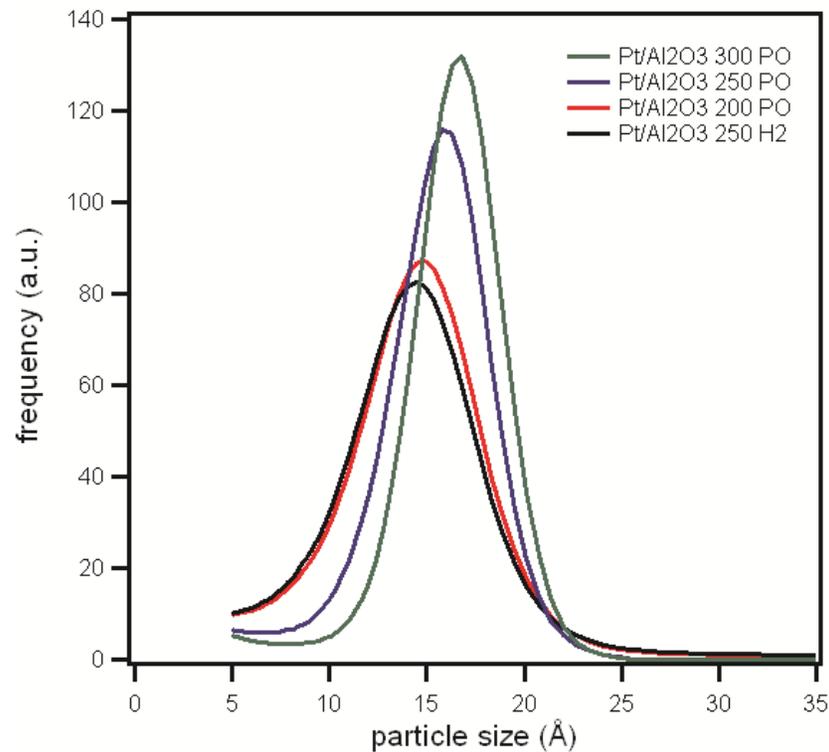
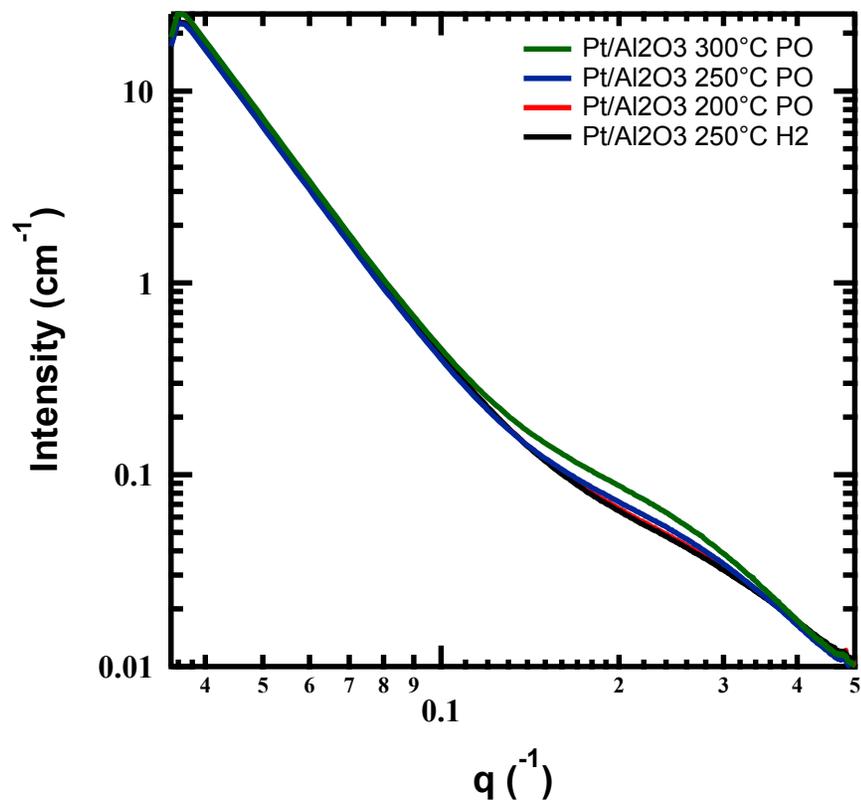
# In-situ experimental setup



Exposure : 1 sec  
Energy (eV): 5 different energies  
EXAFS scan: ~10 min  
Sample: 1.5 mm quartz capillary  
Flow rate: 10 sccm(H<sub>2</sub>/He, propanol/He)



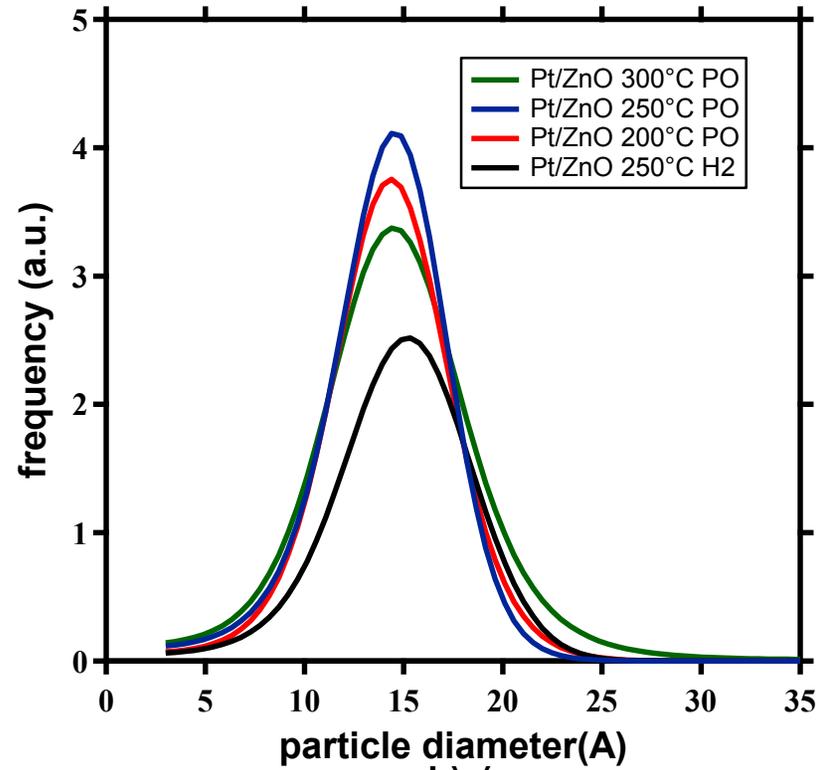
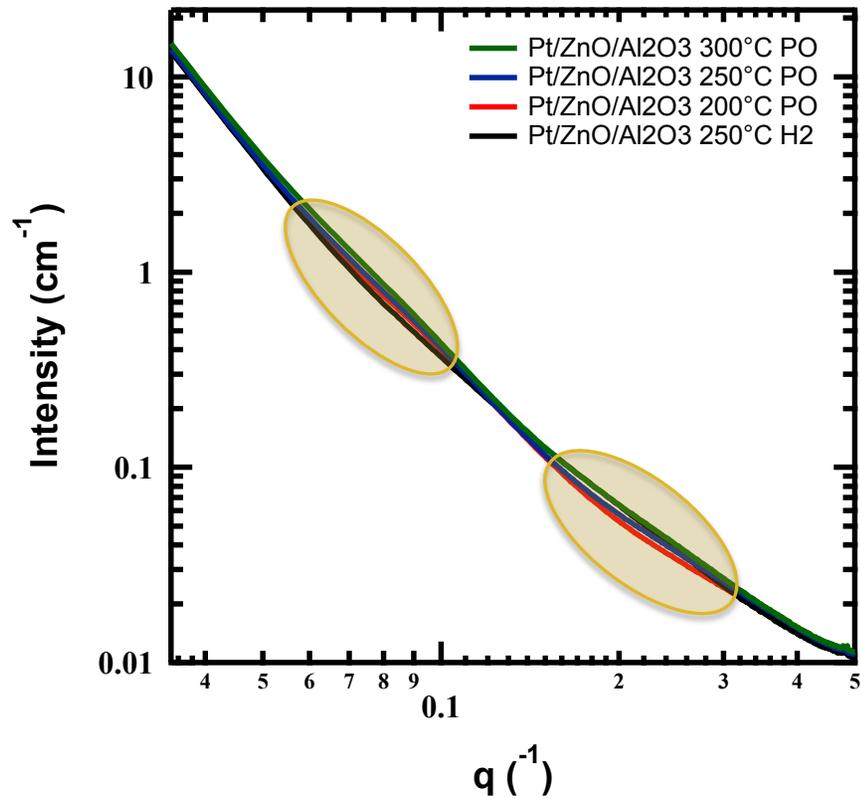
# Pt/Al<sub>2</sub>O<sub>3</sub>



Stable support: simple system, SAXS is not necessary.  
Clear sintering: 14 Å to 17 Å with reactant



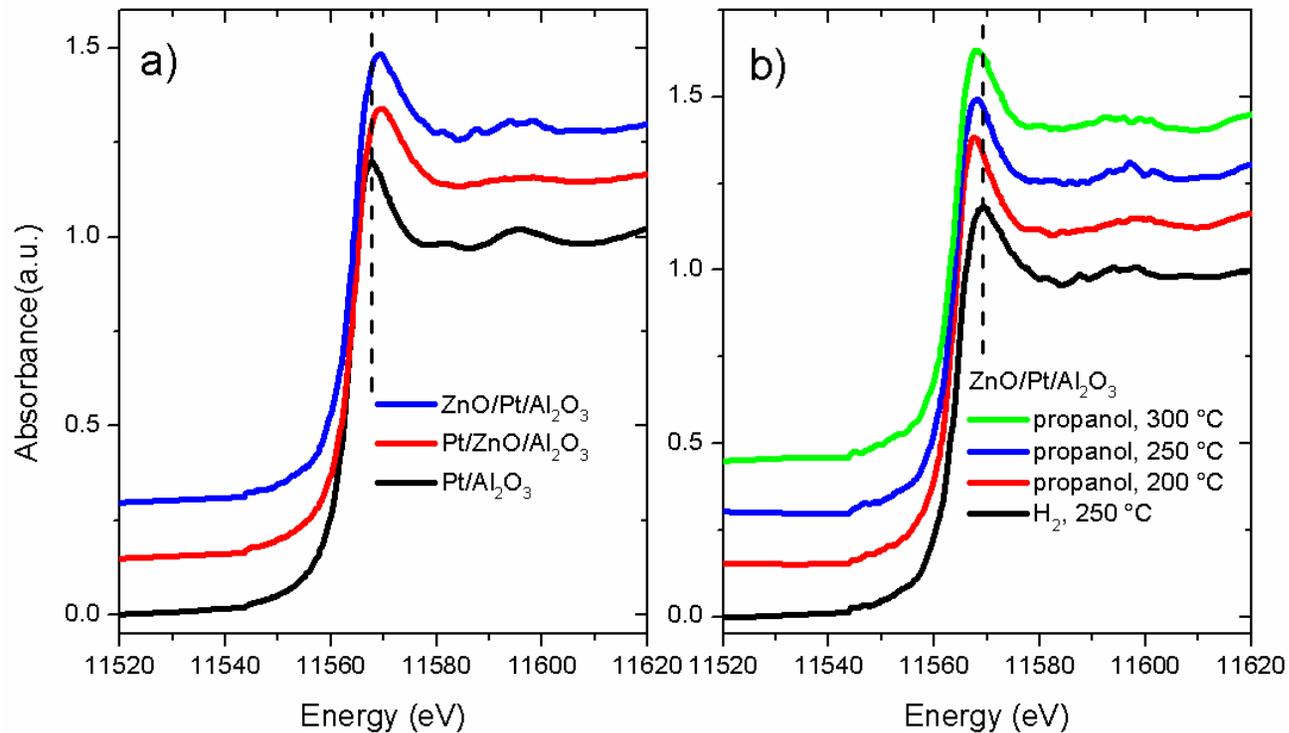
# Pt/ZnO



Complex changes in two regions: sintering to  $> 10$  nm, Pt or Zn ?  
ASAXS result: no change in Pt. ZnO change more dominant



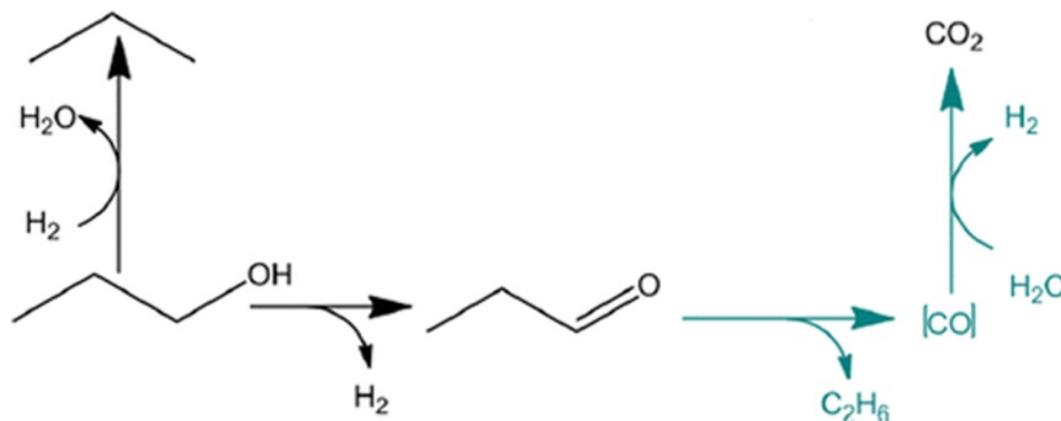
# In-situ XANES: combined with SAXS



**Pt L<sub>3</sub>-edge XANES spectra: charge transfer between Pt-Zn**  
a) after 250 °C H<sub>2</sub> reduction, Pt/Al<sub>2</sub>O<sub>3</sub>, Pt/ZnO/Al<sub>2</sub>O<sub>3</sub> and ZnO/Pt/Al<sub>2</sub>O<sub>3</sub>  
b) during the propanol reforming reaction at 200, 250 and 300 °C on ZnO/Pt/Al<sub>2</sub>O<sub>3</sub>



# 1-propanol reforming for H<sub>2</sub>



Catalyst	rate (mol/ s/g-Pt cat) × 10 <sup>3</sup>	Selectivity at 250 °C (mol%)				
		Ethane	propane	propanal	H <sub>2</sub>	CO <sub>2</sub>
Pt/Al <sub>2</sub> O <sub>3</sub>	7.0	8.9	1.0	2.4	30.4	7.1
Pt/ZnO/ Al <sub>2</sub> O <sub>3</sub>	16.6	3.9	0.1	3.3	53.2	3.9
ZnO/Pt/ Al <sub>2</sub> O <sub>3</sub>	40.0	2.1	0.0	4.1	30.2	3.2



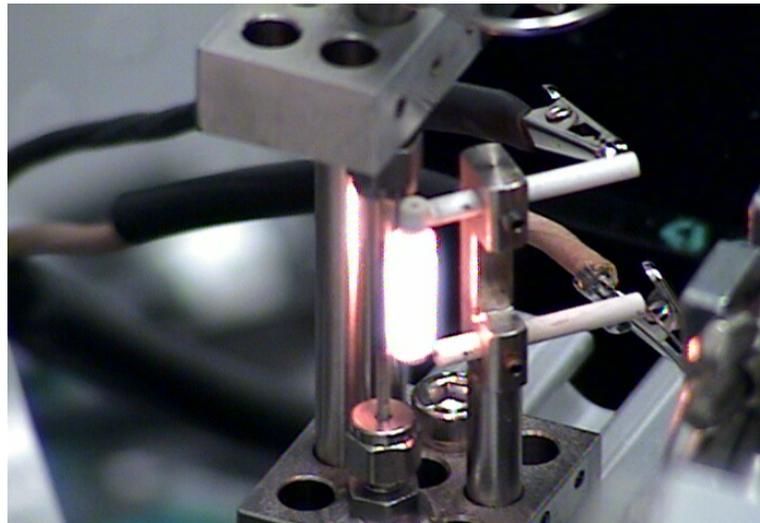
## Summary and future work

- Demonstration of the powerful combination of
    - ALD deposition : nanoscale catalyst synthesis
    - X-ray techniques: ASAXS/XAS
  - Importance of support metal combination
  - Design of new nanocatalyst for biofuel conversion
- 
- Combined SAXS/WAXS
  - In-situ liquid phase reaction



## Extreme condition

- Realistic reaction condition with reaction product analysis: mass, GC/MS
- High pressure high temperature: 1000 psi, 800°C
- In-situ SAXS/WAXS and EXAFS



# Acknowledgement

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  - Junling Lu(ESD,ANL, IACT) - Peter Stair(Chemistry, NW, IACT)
  - Justin Notestein(Chemical and Biological Engineering, NW, IACT)
  - Christian Canlas(Chemical and Biological Engineering, NW, IACT)
  - Kenneth Poepelmeier(Chemistry, NW, IACT) – Linhua Hu(Chemistry, NW, IACT)
- APS
  - Randall Winans
  - Soenke Seifert
  - Byeongdu Lee
  - Xiaobing Zuo

